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A NEW SYNTHESIS OF FLAVONES

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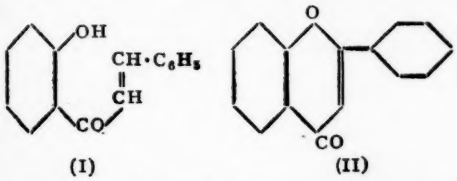
Received July 4, 1949

A number of related groups of compounds having the 15 carbon system, such as anthocyanins and anthoxanthins, occur in nature. The differences between them depend upon the state of oxidation of the oxygen containing ring. Though a large volume of evidence indicates that they have a parallel origin from a common precursor[1] the possibility of one type changing into another does not seem to be altogether excluded. Consequently methods of interconversion have some interest in biogenesis besides their value for the study of structural relations and for the easy synthesis of compounds.

The earliest method of synthesis of flavones employed chalkones (I) as starting materials.[2] This had very limited applicability and alternative methods were therefore preferred. But repeatedly efforts have been made with some success to improve it. The chief defect in the original method of Kostanecki using bromine and chalkones, is the possibility of nuclear bromination and of the predominent tendency to form benzalcoumara-

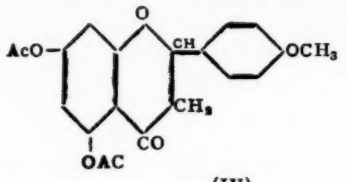


(I) (II) (III)

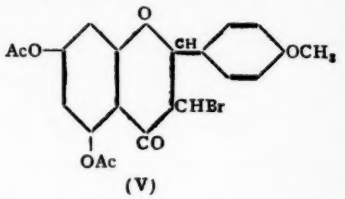
nones[3] (III) instead of flavones (II). A marked improvement is the direct dehydrogenation of chalkones or flavanones by means of selenium dioxide.[4] But it has been found to be satisfactory only in a few simple cases and it seems to fail when the chalkone contains a number of free hydroxyl groups.

In the use of his bromine method Kostanecki[5] met with greater success when he employed flavanones as their methyl ethers. A recent improvement is that of Zemplen and Bognar[6] who have submitted acetates of hydroxyflavanones (IV) to bromination in the presence of ultraviolet light whereby the bromine atom enters the 3-position alone (V). This is subsequently

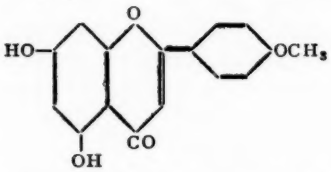
eliminated as hydrogen bromide by means of alcoholic potash. One of their examples employing isosakuranetin diacetate is given below.



(IV)



(V)



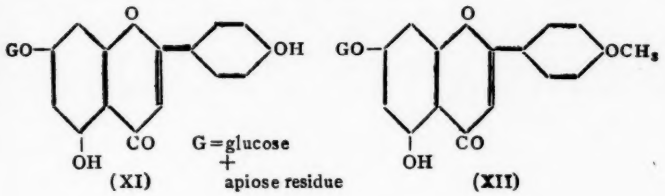
For the dehydrogenation of a flavanone to flavone there is also mention of the use of phosphorus pentachloride. Hattori[7] treated 4′-methoxy flavanone (VI) with phosphorus pentachloride in boiling benzene solution and recorded the preparation of 4′-methoxy flavone (VII). This method has now been repeated by us using 7-methoxy flavanone and the corresponding flavone obtained, the yield being fairly satisfactory. It seemed to be possible that the slow liberation of chlorine from phosphorus pentachloride, at the temperature of boiling benzene employed for this purpose, brought about the dehydrogenating action; but this reagent cannot be used for hydroxy compounds and even in the case of ethers considerable amount of resin formation takes place.

(VI) (VII)

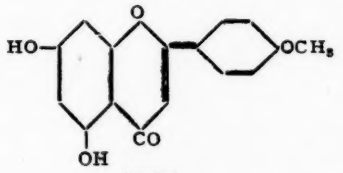
In view of the points discussed above, it appeared that iodine would be a more convenient dehydrogenating agent and it would be free from the defects of nuclear halogenation and resin formation. Actually this reagent has been used earlier for the conversion of rotenone into dehydro-rotenone,[8] but its application has not so far been extended outside the rotenone group, a possible reason being that the discovery was empirical and was made at a time when the existence of a pyranone ring in rotenone was not recognised. It has now been found to be an extremely convenient method of

converting hydroxy flavanones into flavones. In boiling alcoholic solution and in the presence of excess of sodium acetate, iodine brings about smooth dehydrogenation and very good yields of flavones are obtained. Naringenin, isosakuranetin, naringenin dimethyl ether, hesperetin and its dimethyl ether have thus been oxidised and the corresponding flavones prepared and characterised.

The method is suitable also for the oxidation of hydroxyflavanone glycosides. In this connection naringin (VIII), its 4′-monomethyl ether and hesperedin have been used. The first yields a new apigenin-7-glycoside (IX) which when subjected to methylation and hydrolysis gives rise to 7-hydroxy-5: 4′-dimethoxy flavone (X). This is a useful reference compound for establishing the constitution of the 7-glycosides of apigenin; apiin (XI) has now been examined in this connection. Apiin was methylated by Von Gerichten[9] using sodium methoxide and methyl iodide in alcoholic solution. The product was a monomethyl ether (XII) of the glycoside. On hydrolysis it produced a monomethyl ether of apigenin whose constitution was not established by him. Perkin and Horsefall[10] however expressed the opinion that it was probably identical with acacetin (XIII). Accepting this and taking into consideration that the 5-hydroxyl of a flavone is rather resistant to methylation it could be inferred that apiin is a 7-glycoside (XI), the changes being represented as given below.



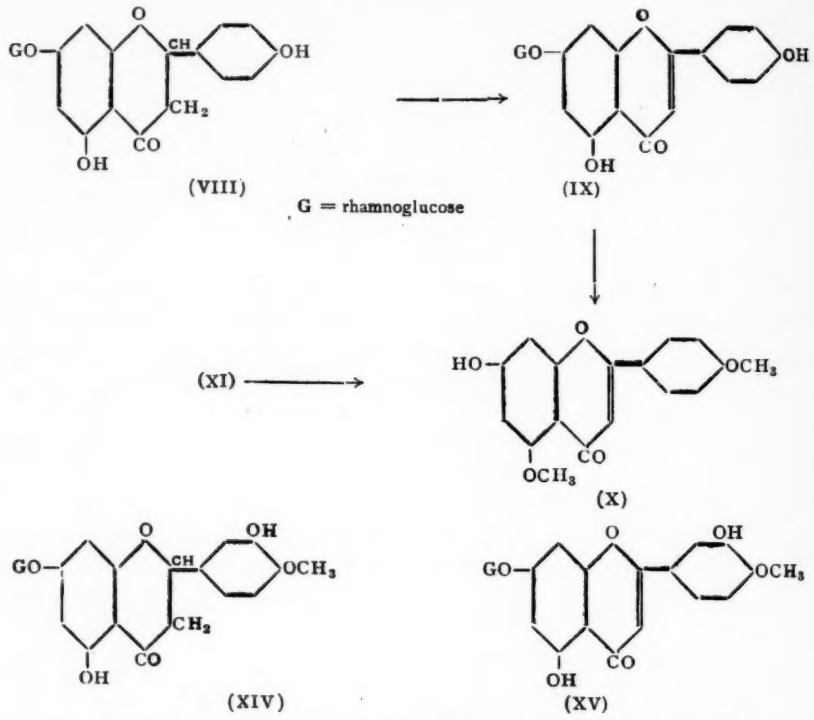
(XI) (XII)



(XIII)

Apiin (XI) has now been subjected to complete methylation and hydrolysis and the product found to be identical with 5: 4′-dimethyl apigenin (X) obtained from naringin as described above. Since the constitution of naringin (VIII) has already been established unequivocally by complete methylation[11] and since the above experiments establish the relationship

between the two glycosides, they provide confirmation of the constitution of apiin. The concerned transformations are represented by the formulæ given below. Though there is no naturally occurring flavone glycoside corresponding to naringin or 4′-methyl-naringin, hesperedin (XIV) gives on oxidation diosmin (XV). This conversion was brought about earlier by Zemplen and Bognar[6] by using their modified bromine method.

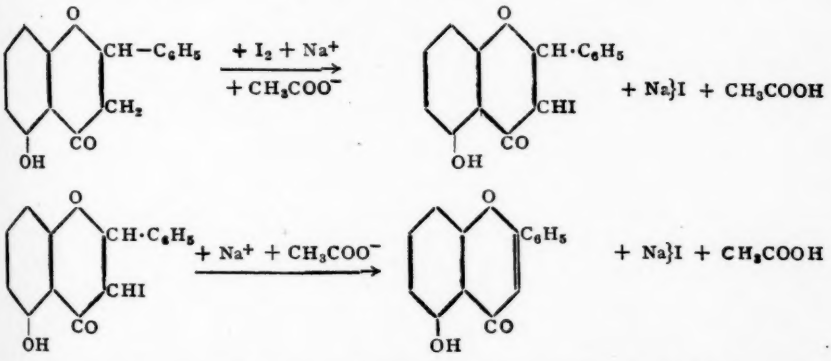


The iodine method of oxidation works most smoothly with all flavanones having a free hydroxyl in the 5-position. If this should be absent or should have been methylated a mixture of products is formed which is sometimes rather difficult to separate unless fairly large quantities are employed. From the mixture some quantity of the chalkone corresponding to the original flavanone could be dissolved out by means of dilute alkali. The remainder contains besides the flavone, the isomeric benzal-coumaranone also. The reason for this difference seems to be the stabilising influence of the 5-hydroxy group on the flavanone structure[11] at the temperature and the mild alkaline conditions employed. It is obvious that with 5-hydroxy compounds

the stable flavanone structure undergoes the normal reaction whereas in the absence of this group, change into the isomeric chalkone is the cause of complications. The influence of temperature is also marked; in the cold more of the flavone is produced and it could be successfully isolated, whereas at the boiling point of alcohol benzalcoumaranone is produced predominantly. This is obvious because of the greater instability of the pyronone ring at the higher temperature.

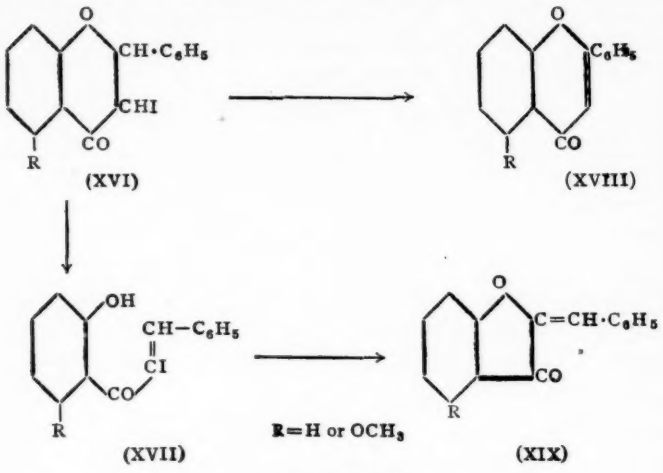
Mechanism of the reaction.—LaForge and Smith[8] considered the dehydrogenation of rotenone as due to iodination and subsequent elimination of hydrogen iodide. This was supported by the fact that they obtained in their experiments only 35% yield of dehydrorotenone the remainder being the acetate of rotenolone. In our experiments on flavanones the yield of flavones was much higher (60–70%). As a by-product small quantities of lower melting substances were found to be formed which appear to be flavanolone acetates thus supporting the general mechanism given by the above authors. These products are being studied in detail and will be reported later.

In considering the details of this chemical reaction it is necessary to emphasise the part played by the unstable and reactive acetate ion, both in the iodination of the reactive CH_2 and subsequent elimination of hydrogen iodide. The stages can be pictured as given below.



In the absence of a hydroxyl group in the 5-position of the flavanone as already mentioned, complicated changes take place due to the instability of the oxygen ring. Some amount of the corresponding chalkone is produced and it does not undergo any iodination; this point was independently tested using 2-hydroxy-4: 6: 4′-trimethoxy-chalkone which was unaffected by iodine. But the flavanone that has undergone iodination (XVI) can

take part in the next stage of the reaction either as such or after the opening of the ring to form the corresponding iodinated chalkone (XVII). In the first case flavone (XVIII) is produced and in the second alternative benzal-coumaranone (XIX) is produced when hydrogen iodide is eliminated.



Experimental

Iodine oxidation of hydroxy flavanones

1. *Naringenin dimethyl ether.*—Naringenin 7 : 4′-dimethyl ether which was prepared by the partial methylation of naringenin[11] (0·5 g.) and sodium acetate (2 g.) were dissolved in hot alcohol (10 c.c.) and the solution kept gently boiling over a small flame. To this a boiling solution of iodine (0·4 g.) in alcohol (8 c.c.) was added slowly. Iodine was rapidly decolourised in the beginning and when the addition was complete there was permanent colour. Even from the hot solution a pale yellow solid separated out. The solution was allowed to cool slowly when more of the compound crystallised out. It was filtered and washed with water. Yield 0·3 g. The product was almost pure and melted at 170–1° with slight sintering at 165°. It crystallised from alcohol in the form of pale yellow prisms melting at 170–1°.[12] It agreed in its properties with apigenin 7 : 4′-dimethyl ether and the mixed melting point with an authentic sample obtained by the partial methylation of genkwanin[13] was undepressed.

2. *Naringenin.*—A boiling solution of naringenin (1 g.) and sodium acetate (3 g.) in alcohol was treated with an alcoholic solution of iodine (0·8 g.) and the solution concentrated on a water-bath till crystals appeared.

The pale yellow solid that separated on cooling was filtered and washed with water. It crystallised from dilute alcohol as almost colourless leaflets melting at 340–42° and was identical in all its properties with apigenin.[12] Yield 0·65 g.

On methylation with excess of dimethyl sulphate and anhydrous potassium carbonate in dry acetone solution, it gave trimethyl apigenin which crystallised from ethyl acetate as colourless rectangular tablets melting at 152–4°[14] and the mixed melting point with a sample obtained by the methylation of genkwanin (described below) was undepressed.

Genkwanin[13] (0·5 g.) was refluxed in acetone solution with dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (2 g.) for 12 hours. It was then filtered and acetone distilled off. The product, genkwanin dimethyl ether, crystallised from ethyl acetate as colourless rectangular tablets melting at 152–4° and was identical with apigenin trimethyl ether.

3. *Isosakuranetin.*—Isosakuranetin which was prepared from naringin by partial methylation and hydrolysis[11] gave acacetin m.p. 258–60°. The mixed melting point with an authentic sample prepared by the Allan-Robinson method[15] was undepressed.

4. *Hesperetin* yielded diosmetin m.p. 256–7°.[16] Its identity was confirmed by preparing the acetate which melted at 193–4°.

5. *Hesperetin dimethyl ether.*—Hesperetin dimethyl ether,[17] prepared by methylating hesperetin with dimethyl sulphate (2·2 mols.) in acetone solution for 8 hours, was treated with iodine as in the case of naringenin dimethyl ether. The solid that separated on cooling the alcoholic solution was filtered and washed with water. It crystallised from alcohol in the form of pale yellow prisms melting at 169–70°. The mixed melting point with the sample of luteolin trimethyl ether described by Rao, Seshadri and Viswanadham[15] was undepressed.

Iodine oxidation of hydroxy flavanone glycosides

1. *Naringin* (VIII) *to Apigenin 7-rhamnoglucoside* (IX).—Naringin (2 g.) was dissolved in alcohol (10 c.c.), sodium acetate (2 g.) added and the solution boiled over a small flame. To this a boiling solution of iodine in alcohol (10 c.c.) was slowly added during the course of 10 minutes. At first there was rapid decolourisation and in the end there was a permanent colouration due to iodine. The solution was then concentrated over a water-bath, diluted with water and saturated with ether. After 24 hours a pale yellow crystalline solid separated out. This was filtered, washed with water and crystallised from alcohol when it came out in the form of

pale yellow flat needles and rectangular plates melting at 198–200°. Its alcoholic solution gave a reddish violet colour with ferric chloride and a deep red colour when reduced with magnesium and hydrochloric acid. (Found: C, 51·1; H, 5·6; $C_{27}H_{30}O_{14}$, $3H_2O$ requires C, 51·3; H, 5·7%.) This was hydrolysed by boiling with 7% aqueous sulphuric acid for 2 hours. The clear solution deposited on cooling apigenin as a pale yellow crystalline solid. It crystallised from alcohol as almost colourless leaflets melting at 340–2° alone or in admixture with the sample obtained from naringenin.

Methylation and hydrolysis to 7-hydroxy-5 : 4'-dimethoxy flavone (X).—The above oxidation product, apigenin glycoside (0·5 g.), was finely suspended in dry acetone (50 c.c.), dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (2 g.) were added and the mixture refluxed for 24 hours. It was then filtered and the potassium salts (R) washed with hot acetone. On evaporating the solvent, a viscous mass was obtained which was insoluble in cold aqueous alkali and gave no colour with ferric chloride in alcohol. It was directly hydrolysed by boiling with 7% aqueous sulphuric acid for 2 hours when a pale yellow solid separated out. It crystallised from alcohol as pale yellow rectangular prisms melting at 265–7°. It dissolved in aqueous sodium hydroxide and carbonate giving a yellow solution. Its alcoholic solution gave no colour with ferric chloride but gave an orange red colour with magnesium and hydrochloric acid.

The potassium salts residue (R) was found to contain further quantities of methylated glycoside. On dissolving it in water and adding sufficient quantity of sulphuric acid, not only to neutralise the carbonate but also to raise the acid concentration to 7% and heating under reflux for 2 hours a crystalline solid was obtained. It melted at 264–6° and was identical with the above product. Total yield 0·15 g. (Found: C, 68·0; H, 4·9; OCH_3, 21·0; $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7, OCH_3, 20·8%.)

On methylation with dimethyl sulphate and anhydrous potassium carbonate in acetone it gave apigenin trimethyl ether, m.p. 152–4°, identical with the sample described already.

Methylation of apiin (XI) and hydrolysis.—A fine suspension of apiin (0·4 g.) in acetone was methylated by refluxing with excess of dimethyl sulphate and anhydrous potassium carbonate for 30 hours. After filtering and distilling off the solvent a pale yellow sticky mass separated which was insoluble in alkali and which gave no colour with ferric chloride in alcohol. It was hydrolysed with 7% sulphuric acid. The product crystallised from alcohol in the form of pale yellow (almost colourless) rectangular prisms and melted at 265–7°. It was identical in its properties and colour reactions

with 7-hydroxy 5:4′-dimethoxy flavone and a mixed melting point with the sample described above was undepressed. As mentioned in an earlier case some more of the product could be obtained by working up the carbonate residues. Total yield 0·1 g.

2. *Naringin-4′-methyl ether.*—This was obtained by partial methylation of naringin with dimethyl sulphate and anhydrous potassium carbonate in acetone.[11]

A solution of naringin-4′-methyl ether in alcohol was treated as before with iodine and sodium acetate. The oxidation product separated only as a semi-solid mass. It did not crystallise satisfactorily and hence was directly hydrolysed to acacetin, m.p. 258–9°. Mixed melting point with an authentic sample was not depressed.

3. *Hesperidin (XIV) to diosmin (XV).*—To a finely divided suspension of hesperidin (2 g.) in alcohol (20 c.c.) was added sodium acetate (3 g.) and the mixture kept gently refluxing over a wire-gauze. To this a boiling solution of iodine (0·8 g.) in alcohol was added and the refluxing continued for further 15 minutes. The solid slowly dissolved and an almost clear solution was obtained. This was filtered hot, and the filtrate concentrated, diluted with water and extracted with chloroform to remove any free iodine. The aqueous solution was then saturated with ether and left overnight. A white crystalline solid gradually separated. It was filtered and washed with water. It crystallised from aqueous pyridine in the form of colourless rectangular plates melting at 270° (decomp.). Its alcoholic solution gave an orange red colour with magnesium and hydrochloric acid. It agreed in all its properties with diosmin.[16]

Methylation and hydrolysis.—As in the previous case, the above oxidation product, diosmin, was methylated in fine suspension in acetone and the product worked up. The aglucone separated after hydrolysis as a pale yellow crystalline solid. It crystallised from alcohol as pale yellow stout rectangular prisms melting at 284–5°. Its alcoholic solution gave no colour with ferric chloride but with magnesium and hydrochloric acid a bright red colour. It agreed in its properties with 7-hydroxy 5:3′:4′-trimethoxy flavone.[18]

Iodine oxidation of fully methylated flavanones:

1. (*a*) 5:7:3′:4′-*Tetramethoxy flavanone.*—As in the above cases a boiling solution of 5:7:3′:4′-tetramethoxy flavanone[19] (0·2 g.) and sodium acetate (1 g.) in alcohol was treated with iodine (0·15 g.). Even from the hot solution a bright yellow solid crystallised out. This was filtered after

cooling and washed with aqueous sodium hydroxide (10%) to remove the chalkone formed (*c*). The undissolved product crystallised from alcohol in the form of bright yellow rectangular rods melting at 171°. Yield 0·06 g. It gave a deep red colour with concentrated sulphuric acid and rapidly decolourised bromine in carbon tetrachloride. It agreed in its properties with 4: 6: 3′: 4′-tetramethoxy benzalcoumaranone described by Geissman and Fukushima[20] and a mixed melting point with a sample obtained by their method was undepressed.

The sodium hydroxide washings (*c*) yielded on acidification the bright yellow chalkone which crystallised from alcohol as bright yellow prisms, m.p. 157–58° and the mixed m.p. with 2-hydroxy-4: 6: 3′: 4′-tetramethoxy chalkone[19] was undepressed.

(*b*) The above reaction was repeated at the room temperature and the reaction mixture was kept constantly shaken for 4 hours. At the end alcohol was removed on a water-bath, the residue treated with hot aqueous alkali (10%), cooled and extracted with ether. On evaporating the ether a pale yellow solid was obtained. Two crystallisations from dilute aqueous alcohol gave the product in almost colourless needles melting at 190–2°. It gave a bright red colour with magnesium and hydrochloric acid in alcoholic solution and agreed in its properties with luteolin tetramethyl ether.[21]

To a boiling solution of 2-hydroxy-4: 6: 4′-trimethoxy-chalkone[11] (0·5 g.) and sodium acetate (2 g.) in alcohol, a solution of iodine in alcohol was added. The colour of iodine was not discharged even after boiling under reflux for two hours; the chalkone could be recovered unchanged.

2. *7-Methoxy flavanone.*—A solution of 7-methoxy flavanone (1 g.) in alcohol (10 c.c.) was treated with shaking with a solution of iodine (0·5 g.) and sodium acetate (2 g.) in alcohol at the room temperature and the product worked up as given in the above experiment. This was twice crystallised from dilute alcohol when it came out in the form of colourless needles melting at 110° and the mixed melting point with an authentic sample of 7-methoxy flavone was not depressed. Yield 0·3 g.

Oxidation with phosphorus pentachloride :

7-Methoxy flavanone.—7-Methoxy flavanone (0·5 g.) was dissolved in hot benzene (10 c.c.) and treated with phosphorus pentachloride (1 g.). The mixture was boiled for 10 minutes. There was a brisk evolution of hydrogen chloride in the beginning which subsided in the end. Benzene was then distilled off and the excess of phosphorus pentachloride was

decomposed with ice. The solid that separated out was filtered and washed with water. On crystallising it from alcohol 7-methoxy flavone was obtained in the form of colourless needles melting at 110–11° and the mixed melting point with an authentic sample was undepressed. Yield 0·15 g.

Summary

Iodine, in the presence of hot alcoholic sodium acetate, is shown to be a convenient reagent for the conversion of hydroxy flavanones into flavones. Naringenin, its 4′ and 4′: 7-dimethyl ethers, hesperetin and its dimethyl ether are thus oxidised smoothly into apigenin and its ethers and diosmetin respectively. The method is also suitable for glycosides; examples chosen are naringin, its monomethyl ether and hesperidin. The constitution of apiin is discussed and confirmed by correlation with that of naringin.

The method works smoothly in all cases where a free hydroxyl is present in the 5-position. In its absence a mixture is formed; by working in the cold the flavones can be obtained, whereas in the hot benzalcoumaranones could be isolated. In such cases the suitability of the phosphorus pentachloride method has been tested using 7-methoxy flavanone.

The reaction is considered to involve (1) iodination of the 3-position and (2) elimination of hydriodic acid and these are brought about smoothly with the help of the active and unstable acetate ions. If the second stage involves iodinated flavanone, flavone is obtained; on the other hand if the corresponding iodinated chalkone is present, benzal-coumaranone results.

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FORMATION OF QUINONES BY OXIDATIVE DEMETHYLATION

Part IV. Isomers of Methyl Pedicinin

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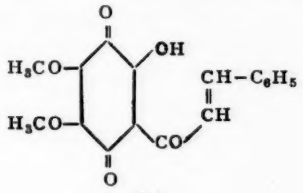
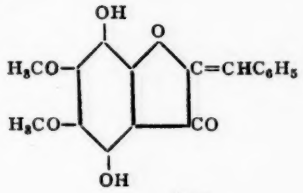
Received July 4, 1949

Closely related to pedicinin is methyl pedicinin. It can be converted into pedicinin by demethylation and could also be obtained from it by methylation. All its properties seem to be very satisfactorily explained by the quinone-chalkone formula, *i.e.*, 2-hydroxy-4: 5-dimethoxy-3: 6-quino-chalkone (I). While discussing the benzal-coumaranone structure for pedicinin (see Balakrishna, Seshadri and Viswanath[1]) it seemed to be relevant to examine a similar structure (II) for methyl pedicinin which was originally proposed for it by Sharma and Siddiqui.[2]



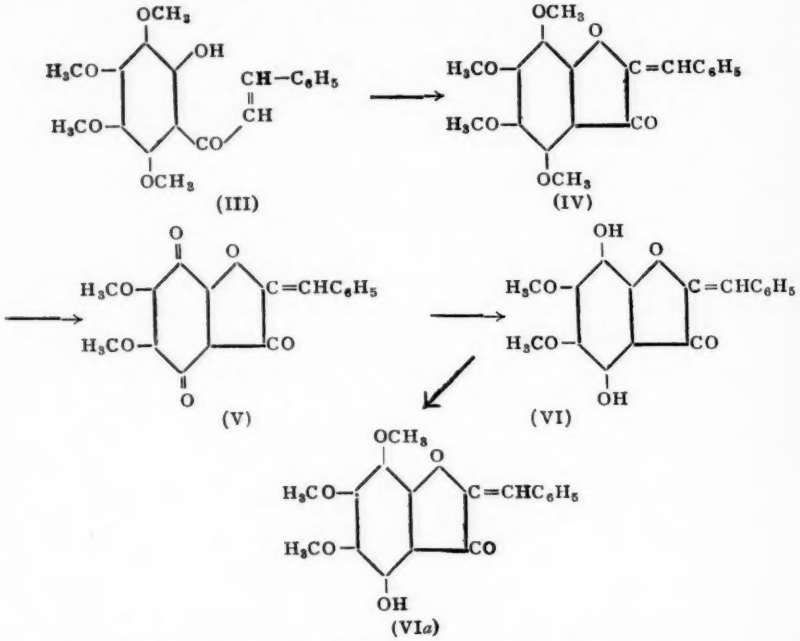
(I)



(II)

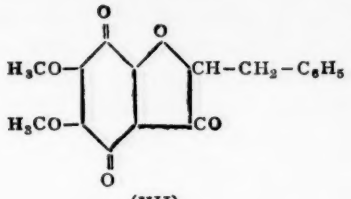
A substance of this constitution has now been synthesised starting from 2-hydroxy-3: 4: 5: 6-tetramethoxy chalkone (III). This readily undergoes change into 4: 5: 6: 7-tetramethoxy-benzal coumaranone (IV) when oxidised with alkaline hyrogen peroxide. A very similar case has been reported recently.[1] The product exhibits all the expected properties, particularly the strong red colour with concentrated sulphuric acid. It undergoes oxidative demethylation with nitric acid yielding 5: 6-dimethoxy-4: 7-quino-benzal coumaranone (V). In this reaction the above tetramethoxy benzal-coumaranone resembles the related 5: 6: 7: 8-tetramethoxy-flavones[3] and flavanones (see also Balakrishna, Seshadri and Viswanath[1]). Simple oxidative demethylation of the para positions takes place and there is no further change. When this quinone is dissolved in sodium hydroxide it gives rise to the corresponding quinol, 4: 7-dihydroxy-5: 6-dimethoxy-benzal-coumaranone (VI). But a more satisfactory method of obtaining

it is to reduce the quinone by means of sulphur dioxide. As a check of its constitution this quinol is subjected to partial methylation; the product is found to be identical with 4-hydroxy 5: 6: 7-trimethoxy-benzal coumaranone (VI *a*) obtained earlier by an independent method.[1]



The quinol (VI) is very different from methyl pedicinin not only in melting point but in other respects too, particularly its colour, solubility and stability in alkali and the mixed melting point (92-96°) was depressed.

Properties	Methyl pedicinin	4 : 7-Dihydroxy-5 : 6-dimethoxy benzal-coumaranone (VI)
Melting point	110–111°	103–4°
Crystal structure ..	Orange prisms	Pale yellow prisms
Solubility in alcohol ..	Fairly soluble	Sparingly soluble
Concentrated sulphuric acid ..	Blood red colour changing to reddish brown	Stable blood-red colour
Behaviour towards sodium hydroxide	Yields pedicinin on acidification of the alkali solution	No change
Sodium bicarbonate ..	Red solution	Insoluble



(VII)

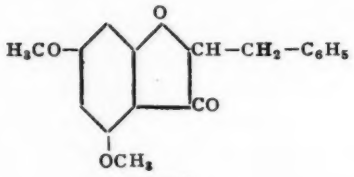
In spite of the intimate relationship between pedicinin and methyl pedicinin, Salooja, Sharma and Siddiqui[4] newly suggested for methyl pedicinin a third formula, benzyl-quino-coumaranone (VII) which does not have a parallel in any of the formulæ proposed for pedicinin. In justification of this they pointed out that it dissolves in sodium bisulphite and gets reduced by it more readily than pedicinin, that it is saturated to bromine and on catalytic reduction with platinum black it absorbs two hydrogen atoms only. They, however, realised that methyl pedicinin dissolves readily in sodium or potassium bicarbonate and gives also phenolic colour reactions with alcoholic ferric chloride. These, however, were considered by them to be apparent discrepancies in the behaviour of methyl pedicinin and were explained by assuming that under the influence of certain reagents it isomerises into the rather unstable benzal-coumaranone structure (II) originally proposed by Sharma and Siddiqui. The proposal of this isomeric change for which no analogies seem to exist, is now clearly not valid because it has been shown in the foregoing pages that 5: 6-dimethoxy-4:7-dihydroxy-benzal-coumaranone exhibits considerable stability in the presence of alkali and other reagents. But one general point which could be considered in this connection is the possible existence of chalkone-benzylcoumaranone interconversion just like the chalkone-flavanone interconversion. The former does not seem to have been met with though the latter is familiarly known. Since no information is available regarding the properties of benzyl-coumaranones, attempts have now been made to prepare some of them and study their properties and if possible to prepare a compound of the structure suggested by Salooja, Sharma and Siddiqui for methyl pedicinin. In this effort we have been successful and the results are discussed below.

For the synthesis of benzyl-coumaranones the reduction of the corresponding benzal-coumaranones with hydrogen at a pressure of 2 to 3 atmospheres in the presence of platinum oxide was adopted by Drumm, Macmahon and Ryan,[5] but Freudenberg, *et al.*[6] reported that side reactions occurred with the above catalyst and hence used nickel on kieselghur for the reduction. An independent method for the synthesis was reported by Shriner and Damschroder.[7] They condensed the appropriate phenol ether

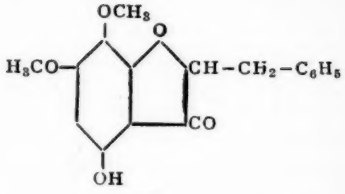
and α-bromo-β-phenyl-propionyl-chloride in the presence of anhydrous aluminium chloride in carbon disulphide medium. Thus they synthesised 6-methoxy-benzyl-coumaranone, which was obtained as colourless crystals melting at 92-94°. Further, another method involving direct benzylation of a coumaranone using sodium methoxide and benzyl chloride was also attempted by them without success.

Of the above methods the one selected now as most convenient is that of Shriner and Damschroder with the modification that cold ether is used instead of carbon disulphide as solvent. α-Bromo-β-phenyl-propionyl-chloride is condensed first with fully methylated resorcinol and phloroglucinol ethers. When the products are heated with sodium acetate solution, 6-methoxy- and 4: 6-dimethoxy-benzyl-coumaranones (VIII) are obtained. The former has the same melting point as given by Shriner and Damschroder. These benzyl-coumaranones are colourless crystalline compounds which do not give any colour with alcoholic ferric chloride and are insoluble in aqueous sodium hydroxide. With concentrated sulphuric acid they form yellow solutions. They are stable to treatment with cold alcoholic potash (10%, half an hour) and can be recovered unchanged on dilution with water.

1:2:3:5-Tetramethoxy-benzene undergoes the same condensation forming 4-hydroxy-6: 7-dimethoxy-benzyl coumaranone (IX). The partial demethylation in the course of this condensation seems to be peculiar to this particular case. It is explicable on the basis that the benzyl coumaranone ring closes up rather readily during the course of the first stage of the condensation and the 4-position of the coumaranone undergoes demethylation in the presence of the aluminium chloride still present.



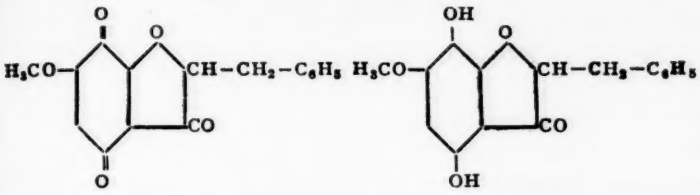
(VIII)



(IX)

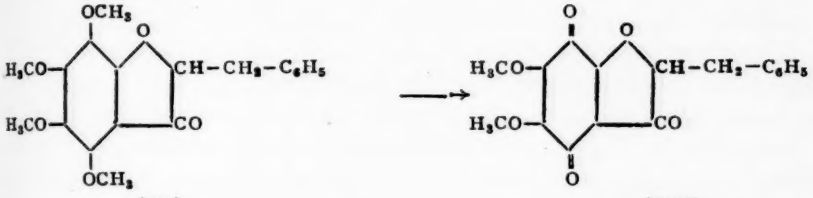
The above compound (IX) suffers oxidative demethylation with nitric acid readily forming 6-methoxy-4: 7-quino-benzyl-coumaranone (X). It could be reduced to the corresponding quinol (XI) which is stable in cold aqueous alkali and does not undergo isomeric change.

As a next stage 4: 5: 6: 7-tetramethoxy benzyl-coumaranone (XII) was prepared starting from pentamethoxy benzene (Baker).[8] By the action



(X) (XI)

of nitric acid it underwent change into the corresponding 5: 6-dimethoxy-4: 7-quino-benzyl-coumaranone (XIII), the required isomer of methyl pedicinin. It melts at 127-28° which is much higher than the melting point of methyl pedicinin. It could be reduced to the corresponding quinol. It does not dissolve in sodium carbonate and bicarbonate and does not undergo change into pedicinin in the presence of mineral acids and does not give any ferric chloride colour. Hence methyl pedicinin cannot be given the constitution of this compound.



(XII) (XIII)

Properties	Methyl pedicinin	4 : 7-quino-5 : 6-dimethoxy-benzyl coumaranone (XIII)
Melting point	110–11°	127–28°
Crystal structure ..	Orange prisms	Yellow prisms
Concentrated sulphuric acid ..	Blood-red colour changing to reddish brown	Yellow
Behaviour towards sodium hydroxide	Yields pedicinin on acidification	Dissolves
Sodium bicarbonate ..	Red solution	Insoluble

From the above study it has to be concluded that the quino-chalkone formula (I) is the only correct one for methyl pedicinin as the other alternative formulæ represent substances of very different properties. Further the possibility of reversible isomeric change between chalkones and benzyl-coumaranones does not find experimental support.

Experimental

5 : 6-*Dimethoxy*-4 : 7-*quino-benzal-coumaranone* (*V*)

I stage.—2-Hydroxy-3 : 4 : 5 : 6-tetramethoxy-chalkone (III) was originally prepared by the partial methylation of despedicellin.[3] For the present work it was obtained by the condensation of 2-hydroxy-3 : 4 : 5 : 6-tetramethoxy-acetophenone[8] with benzaldehyde in the presence of alcoholic potash. It was in the form of thick orange yellow oil and was characterised by conversion into the corresponding 5 : 6 : 7 : 8-tetramethoxy-flavanone melting at 78-79°.

The above chalkone (5 c.c.) was dissolved in alcohol (50 c.c.) and treated in small quantities with sodium hydroxide (6%; 15 c.c.) and hydrogen peroxide (6%; 10 c.c.) alternately, all the while shaking the mixture vigorously. The mixture was set aside for two hours. It was then diluted with water and extracted with ether. When the ether extract was concentrated, a deep orange liquid (4 c.c.) separated out. It did not solidify at room temperature. With alcoholic ferric chloride it did not give any colour and was insoluble in sodium hydroxide. With concentrated sulphuric acid it formed a blood-red solution. This sample of tetramethoxy benzal-coumaranone (IV) was used directly for the following reaction.

II stage.—The above tetramethoxy compound (4 c.c.) was treated with nitric acid (20 c.c.; d. 1·2) in the cold (20-25°) for 15 minutes and the solution diluted with water. The brown solid that separated out was filtered and crystallised from alcohol. It was obtained as light orange prisms melting at 188-89°. Yield 0·8 g. (Found: C, 65·3; H, 4·1; $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·8%.) With alcoholic ferric chloride it did not give any colour.

4 : 7-*Dihydroxy*-5 : 6-*dimethoxy-benzal-coumaranone* (*VI*)

Sulphur dioxide was passed through an alcoholic suspension of the above quinone (0·5 g.) for 15 minutes. When the solution was clear it was concentrated on a boiling water-bath and the product allowed to crystallise, the dihydroxy compound being obtained as small yellow prisms melting at 103-104°. Yield, 0·2 g. (Found: C, 65·2; H, 4·8; OCH_3, 20·2; $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5; OCH_3, 19·8%.) With alcoholic ferric chloride it gave a brown colour and was soluble in aqueous alkali. It was insoluble in sodium carbonate and bicarbonate solutions. With concentrated sulphuric acid it gave a blood-red colour. The mixed melting point with an authentic sample of methyl pedicinin was depressed (92-96°).

The dihydroxy compound could also be prepared by the following method. The above quinone (0·2 g.) was treated with sodium hydroxide

(20%; 10 c.c.). It went into solution on warming. After allowing it to stand at room temperature for 15 minutes the solution was acidified with sulphuric acid and the separated solid filtered. It crystallised from alcohol in small yellow prisms and was identical in all respects with the dihydroxy compound obtained above; the mixed melting point was undepressed.

4-Hydroxy-5: 6: 7-trimethoxy-benzal-coumaranone (VI a)

The above dihydroxy compound (VI) (0·2 g.) was dissolved in dry acetone (25 c.c.) and anhydrous potassium carbonate (5·0 g.) and dimethyl sulphate (0·1 c.c.) were added. The mixture was refluxed for six hours and the potassium salts were filtered off. The acetone filtrate was concentrated on a boiling water-bath. The residue crystallised from alcohol as yellow stout rectangular plates melting at 152-53°. It was identical with the partial methyl ether obtained from 4: 5: 7-trihydroxy-6-methoxy-benzal coumaranone[1] in all respects; the mixed melting point was undepressed.

6-Methoxy-benzyl-coumaranone

This was prepared by a slight modification of the method of Shriner and Damschroder.[7]

α-Bromo-β-phenyl-propionyl-chloride required for this purpose was made by the method of Fischer.[9] It distilled at 132-33° under 12 mm. pressure and had all the properties described by Fischer.

O-Dimethyl-resorcinol (5 c.c.) was dissolved in dry ether (50 c.c.) and cooled in ice. Anhydrous aluminium chloride (20 g.) was added in small lots and the mixture was treated with the above acid chloride (7 c.c.) with vigorous shaking. It was allowed to stand overnight at the room temperature. Water (50 c.c.) and concentrated hydrochloric acid (50 c.c.) were added alternately in small quantities with shaking and cooling under the tap and the mixture was heated on a boiling water-bath for half an hour. The liquid that separated out was extracted with ether. After distilling off the ether, the residue was boiled with sodium acetate (10%) solution. The semi-solid that separated out on cooling was crystallised first from alcohol and then from petroleum ether. It was obtained as colourless rectangular prisms melting at 94-95°. (Found: C, 75·2; H, 5·6; $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%.) With alcoholic ferric chloride it did not give any colour and was insoluble in aqueous sodium hydroxide.

4: 6-*Dimethoxy-benzyl-coumaranone (VIII)*

O-Trimethyl phloroglucinol (4·0 g.) was dissolved in dry ether (50 c.c.) and treated with anhydrous aluminium chloride (15 g.) and α-bromo-β-phenyl-propionyl chloride (6 c.c.). The reaction was carried out and the product

worked up as in the above experiment. It crystallised from petroleum ether as colourless prisms melting at 105-6°. (Found: C, 72·0; H, 5·4; $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%.) With alcoholic ferric chloride it did not give any colour and was insoluble in aqueous sodium hydroxide.

4-*Hydroxy*-6: 7-*dimethoxy-benzyl-coumaranone* (*IX*)

To an ice-cooled dry ether solution of 1:2:3:5-tetramethoxy-benzene (15 c.c.) anhydrous aluminium chloride (25 g.) was added in small lots. α-Bromo-β-phenyl-propionyl-chloride (7 c.c.) was then added and the reaction mixture was allowed to stand overnight. The product was worked up as in similar experiments described above. When crystallised twice from methyl alcohol it was obtained as shining colourless hexagonal plates melting at 97-98°. (Found: C, 68·4; H, 5·0; $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%.) With alcoholic ferric chloride it gave a brown colour and was sparingly soluble in aqueous alkali. It gave an yellow colour with concentrated sulphuric acid.

On methylation with dimethyl sulphate and anhydrous potassium carbonate in dry acetone medium it gave the completely methylated compound. The trimethyl ether was a liquid at room temperature and did not give any colour with alcoholic ferric chloride and was insoluble in aqueous alkali.

4: 7-*Quino*-6-*methoxy-benzyl-coumaranone* (*X*)

The above compound (IX) (0·5 g.) was treated with nitric acid (5 c.c.; d., 1·2) in the cold (15-20°) for 15 minutes and the product worked up as in similar cases. It crystallised from alcohol as yellow prisms melting at 115-16° (Found: C, 67·4; H, 4·4; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2%.) With concentrated sulphuric acid it gave an orange colour.

6-*Methoxy*-4: 7-*dihydroxy-benzyl-coumaranone* (*XI*)

The above quinone (0·2 g.) was reduced with sulphur dioxide in alcoholic solution. On concentrating the solution, the dihydroxy compound crystallised as yellow short needles melting at 87-88°. (Found: C, 66·9; H, 5·1; $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9%.) With alcoholic ferric chloride it gave a reddish-brown colour and formed an yellow solution with aqueous alkali. With concentrated sulphuric acid it gave an yellow colour.

5: 6-*Dimethoxy*-4: 7-*quino-benzyl-coumaranone* (*XIII*)

Pentamethoxy-benzene[8] (6·0 c.c.) was treated with anhydrous aluminium chloride (30 g.) and α-bromo-β-phenyl-propionyl-chloride (5 c.c.),

carefully in an ice-cooled dry ether (100 c.c.) medium. The mixture was allowed to stand overnight. Water (100 c.c.) and concentrated hydrochloric acid (50 c.c.) were added carefully and the ether was allowed to distil off. The mixture was heated at 100° on a boiling water-bath for 15 minutes. On cooling, an oily layer separated out. It was extracted with ether and the ether distilled off. The liquid that was left behind was boiled with aqueous sodium acetate (10%). On cooling a dark-coloured oily layer separated out. It was extracted with ether and the ether solution dried over anhydrous sodium sulphate. Removal of ether by distillation left behind a liquid which did not solidify at room temperature. So it was directly treated with nitric acid (10 c.c.; d., 1·2) in the cold (15-20°) for 15 minutes. On diluting the solution and working up the product that separated out, the quinone crystallised from methyl alcohol as yellow prisms melting at 127-28°. (Found: C, 65·2; H, 4·6; $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5%.) With alcoholic ferric chloride it did not give any colour and formed an yellow solution with concentrated sulphuric acid. It was insoluble in sodium carbonate and bicarbonate solutions, but slowly dissolved in aqueous sodium hydroxide.

When sulphur dioxide was passed for 15 minutes through an alcoholic solution of the quinone and the solution concentrated, an yellow solid was obtained. It crystallised from alcohol as yellow rectangular plates melting at 120-21°. With alcoholic ferric chloride it gave a reddish-brown colour and was converted back to the quinone by the action of *p*-benzoquinone in absolute alcoholic medium.

Summary

Two isomers of methyl pedicinin are synthesised and studied: (1) 4: 7-dihydroxy-5: 6-dimethoxy-benzal-coumaranone and (2) 5: 6-dimethoxy-4: 7-quino-benzyl-coumaranone. The first is made from 2-hydroxy-3: 4: 5: 6-tetramethoxy-chalkone by conversion into the corresponding benzal-coumaranone, oxidative demethylation to 4: 7-quinone and reduction to the quinol. The second synthesis condenses pentamethoxy-benzene with α-bromo-β-phenyl-propionyl chloride to yield tetramethoxy-benzyl-coumaranone and oxidises it with nitric acid to the quinone. Their properties are different from methyl pedicinin and they do not undergo conversion into it. It is therefore concluded that methyl pedicinin should be given only the quinone chalkone formula and that the alternative formulations are not valid. Further the possibility of reversible isomeric change between chalkones and benzylcoumaranones does not find experimental support.

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THE ELASTIC CONSTANTS OF SODIUM TARTRATE AND ROCHELLE SALT

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1. Introduction

Sodium tartrate, $Na_2C_4H_4O_6\ 2H_2O$, is a piezo-electric crystal belonging to the orthorhombic system, possessing very interesting properties like its analogue, Rochelle salt. The elastic, piezo-electric and dielectric properties have been extensively studied for Rochelle salt because of its many practical applications. Regarding the elastic constants, not only Rochelle salt as such but also the salt resulting after replacing the potassium ion by ammonium ion has been studied (Mandell, 1928). The results are summarised by Wooster (1938) and Cady (1946).

A large amount of Raman effect data of Rochelle salt, potassium and sodium tartrates is available in the literature from the investigations of Gupta (1938), Canals and Peyrot (1938), Nedungadi (1941) and more recently by Padmanabhan (1948). The three substances exhibit an interesting gradation in their properties.

An important fact observed during the comparative studies of the piezo-electric property is the marked decrease in the piezo-electric constants when the potassium ion is replaced by ammonium ion in Rochelle salt. The elastic constants are also found to have remarkably changed; and this indicates that an extension of similar studies with sodium tartrate might also yield useful information. The determination of the complete set of elastic constants of sodium tartrate and also incidentally of Rochelle salt, employing one and the same method for both is therefore considered desirable and the results of the investigation are given in the following sections.

2. The Elastic Constants of the Orthorhombic System

The system has nine independent constants, C_{11}, C_{22}, C_{33}, C_{12}, C_{13}, C_{23}, C_{44}, C_{55} and C_{66}. The crystallographic axes *a*, *b*, *c* form the orthogonal axial system of reference X_1, X_2, X_3. To get all the constants, various sections with different orientations are necessary. The appropriate constants of each section are determined by the normal to the surface of the section; and for the simple axial cuts, they can be very easily derived from Christoffel's equations. But, for the others, the approximate method would be to use

the tensor transformation of the appropriate constant. For the longitudinal mode, we get the effective elastic constant from the constant C_{33}' where the direction is denoted by the X_3' axis defined by the direction cosines a_{13}, a_{23}, a_{33}.

$$C_{33}' = a_{13}^4 c_{11} + a_{23}^4 c_{22} + a_{33}^4 c_{33} + 2a_{13}^2 a_{23}^2 (c_{12} + 2c_{66}) + 2a_{23}^2 a_{33}^2 (c_{23} + 2c_{44}) + 2a_{33}^2 a_{13}^2 (c_{13} + 2c_{55}) \quad (1)$$

Using Christofel's equations for the axial cuts to get the torsional constants and equation (1) for the rest, we get the effective constants for the various plates as summarised in Table I below:—

TABLE I

Plate No.	Direction cosines of the normal to the plate			Effective elastic constants	
	a_{13}	a_{23}	a_{33}	Longitudinal	Torsional
1	1	0	0	C_{11}	C_{55} and C_{66}
2	0	1	0	C_{22}	C_{66} and C_{44}
3	0	0	1	C_{33}	C_{44} and C_{55}
4	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0	${}_4C'_{33} = \frac{1}{4}(C_{11}+C_{22}+2C_{12}+4C_{66})$	..
5	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	${}_5C'_{33} = \frac{1}{4}(C_{22}+C_{33}+2C_{23}+4C_{44})$	..
6	$\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$	${}_6C'_{33} = \frac{1}{4}(C_{33}+C_{11}+2C_{13}+4C_{55})$	..
7	$\frac{\sqrt{3}}{2}$	$\frac{1}{2}$	0	${}_7C'_{33} = \frac{1}{16}(9C_{11}+C_{22}+6C_{12}+12C_{66})$	..
8	0	$\frac{\sqrt{3}}{2}$	$\frac{1}{2}$	${}_8C'_{33} = \frac{1}{16}(9C_{22}+C_{33}+6C_{23}+12C_{44})$	..
9	$\frac{1}{2}$	0	$\frac{\sqrt{3}}{2}$	${}_9C'_{33} = \frac{1}{16}(9C_{33}+C_{11}+6C_{13}+12C_{55})$	..

Hence the first six sections are sufficient to determine all the nine constants. The last three can be used as checks. For sodium tartrate, all the nine sections are used; while for Rochelle salt, only the first six have been utilized.

The suffix on the left of C'_{33} indicates the plate number. For the last six sections, only the longitudinal modes have been used in the investigation.

3. Experimental Technique

Large single crystals of sodium tartrate and Rochelle salt were grown from aqueous solutions of the salts. All specimens used were flawless, with the usual prominent faces and pinacoids well developed so that the axes could be easily determined and confirmed by examining them between crossed polaroids. The crystallographic data provided by Groth and more

especially by Cady (1946) concerning Rochelle salt are used to identify the *a*, *b* and *c* axes. The necessary sections were cut by using an accurate goniometer. The angles are accurate within $\pm 1°$.

The experimental technique and the arrangement in general are the same as the ones described by the author in a previous publication (1948). But, since the crystals are piezo-electric by themselves, wherever possible, the plates of sodium tartrate are directly excited by putting them between the condenser plates in parallel with the variable condenser of the oscillator circuit and in very close contact with the plates. They were later repeated by driving them with a separate Z-cut tourmaline plate as usual. The measurements agreed within 3%, the difference probably being due to the piezo-electric effects. Thus six of the nine plates of sodium tartrate have been worked both by direct and indirect excitation. The axial cuts could not be directly worked and this might be attributed to the lack of a non-zero piezo-electric modulus for the thickness oscillations of the axial cuts, in analogy with Rochelle salt.

However, the piezo-electric corrections are very largely minimised in the technique of indirect excitation; for, in that case, the crystal plate is completely short-circuited by the thin tin foil which covers both sides of the plate and makes electrical contact between the tourmaline driver and the condenser plates. This effective short circuiting prevents polarisation of the crystal plate.

All the sections of Rochelle salt are indirectly worked to avoid heating effects and also the consequent damage to the plates that occurs when excited directly.

All the results given in the next section are from indirect excitation.

4. Experimental Observations and Results

During the oscillations of the crystal plate when excited directly, it was kept well within the liquid in the cell in which the waves are impressed to obtain the Debye-Sears' phenomenon by which they are detected. This minimizes the heating effect in the crystal plate to a large extent, since the heat produced is not localized as it would be if the surface of the crystal just touches the liquid as it does when it is indirectly excited. Nevertheless, due to occasional and stray " booms " of the oscillator, the amplitude of the oscillations goes so high that the plate is heated considerably. When this happened, the plate broke with a peculiar hissing sound and the oscillator is totally damped out. Even when the plate was not broken, the damping of the oscillator had been complete when the heating took place. This

might be attributed to the conductivity of the crystal rising considerably due to heating, in a manner analogous to the effect of heating of Rochelle salt. In the latter case, it is well known that beyond about 30° C. the conductivity rises enormously (Wooster, p. 214). A similar effect taking place in sodium tartrate also means that the variable condenser in the tank circuit is effectively short-circuited since the plate becomes more of a conductor than a dielectric and the condensor having it in between is in parallel with the variable condenser of the oscillator. But, if the plate is not broken down completely it is observed that after a few hours it recovers and the frequency measurements are found to be the same after recovery showing that the internal structure remains unaffected. In all such cases, the observations are repeated after 24 hours interval for recovery.

Mention may be made that in the direct excitation, the even harmonics of the fundamental modes also appeared, though with very much feebler intensity than the odd harmonics. This is in conformity with the observations made in other piezo-electric substances like quartz and tourmaline, where, theoretically speaking, the even harmonics should not appear. But practically they do occur due, perhaps, as Bergmann (1939) puts it, to the inhomogeneous local variations in the plates or the non-uniformity of the electric field at the edges, etc.

As Rochelle salt was worked completely indirectly, no such difficulties were encountered in that case.

The quantitative results are given in the following tables.

TABLE II. *Sodium tartrate*

Density = 1·794 gm./cm.^{3}

Plate No.	Description of the plate	Thickness in mm.	Mode and effective elastic constant	Frequency in Mc./sec.	Value of the effective elastic constant 10^{11} dynes/cm.^{2}
1	X_1-cut	1·51	C_{11} (l)	1·679	4·609
1	,,	,,	C_{55} (t)	0·4339	0·3082
1	,,	,,	C_{66} (t)	0·7775	0·9895
2	X_2-cut	1·135	C_{22} (l)	2·433	5·473
2	,,	,,	C_{44} (t)	1·16	1·245
2	,,	,,	C_{66} (t)	1·028	0·977
3	X_3-cut	1·42	C_{33} (l)	2·143	6·646
3	,,	,,	C_{44} (t)	0·926	1·241
3	,,	,,	C_{55} (t)	0·4632	0·3106
4	(45, 45, 0)	1·50	$_4C'_{33}$ (l)	1·794	5·2
5	(0, 45, 45)	1·35	$_5C'_{33}$ (l)	2·15	6·044
6	(45, 0, 45)	1·44	$_6C'_{33}$ (l)	1·79	4·95
7	(60, 30, 0)	1·485	$_7C'_{33}$ (l)	1·731	4·742
8	(0, 60, 30)	1·48	$_8C'_{33}$ (l)	1·803	5·112
9	(30, 0, 60)	1·45	$_9C'_{33}$ (l)	1·901	5·455

TABLE III. *Rochelle salt*

Density 1·791 gm./cm.³

Plate No.	Description of the plate	Thickness in mm.	Mode and the effective constant	Frequency in Mc./sec.	Value of the constant in 10^{11} dynes/cm.²
1	X_1-cut	1·24	C_{11} (*l*)	1·920	4·056
1	,,	,,	C_{55} (*t*)	0·5152	0·292
1	,,	,,	C_{66} (*t*)	0·9274	0·947
2	X_2-cut	1·27	C_{22} (*l*)	2·123	5·203
2	,,	,,	C_{44} (*t*)	1·03	1·225
2	,,	,,	C_{66} (*t*)	0·904	0·944
3	X_3-cut	1·28	C_{33} (*l*)	2·335	6·396
3	,,	,,	C_{44} (*t*)	1·021	1·223
3	,,	,,	C_{55} (*t*)	0·5108	0·306
4	(45, 45, 0)	1·02	${}_4C'_{33}$ (*l*)	2·469	4·541
5	(0, 45, 45)	1·25	${}_5C'_{33}$ (*l*)	2·262	5·724
6	(45, 0, 45)	1·05	${}_6C'_{33}$ (*l*)	2·425	4·642

In the above tables, (*l*) and (*t*) respectively indicate the longitudinal and torsional modes.

Using the relations developed in the previous section, we can therefore calculate all the nine constants for both the crystals. Table IV below gives the elastic constants in units of 10^{11} dynes/cm.² thus calculated for both, and correct to 2 decimal places.

TABLE IV

Substance	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
Sodium tartrate ..	4·61	5·47	6·65	1·24	0·31	0·98	2·86	3·20	3·52
Rochelle salt ..	4·06	5·20	6·40	1·22	0·30	0·95	2·56	3·46	3·20

The elastic moduli, *s*'s are also calculated, using the conversion formulæ (Voigt) of the type

$$\sigma s_{11} = \begin{vmatrix} c_{22} & c_{23} \\ c_{23} & c_{33} \end{vmatrix} ; \qquad \sigma s_{23} = \begin{vmatrix} c_{31} & c_{32} \\ c_{11} & c_{12} \end{vmatrix} ; \qquad s_{44} = \frac{1}{c_{44}}, \text{ etc.}$$

where

$$\sigma = \begin{vmatrix} c_{11} & c_{12} & c_{13} \\ c_{12} & c_{22} & c_{23} \\ c_{13} & c_{23} & c_{33} \end{vmatrix}$$

It must of course be noted that $C_{ij} = C_{ji}$ in the above formulæ. The values of the elastic moduli are given in the table below:—

TABLE V

Substance	s_{11}	s_{22}	s_{33}	s_{44}	s_{55}	s_{66}	s_{12}	s_{13}	s_{23}
1 Sodium tartrate	37·1	31·6	26·4	80·6	323	100	−12·0	−11·5	−10·9
2 Rochelle salt ..	50·2	30·4	31·7	82·0	333	106	−11·6	−21·4	−8·95

The linear compressibilities β_1, β_2, β_3 along the principal directions X_1, X_2, X_3 and the volume compressibility β in the above units are also calculated using the relations

$$\beta_1 = s_{11} + s_{12} + s_{13} \qquad \beta_2 = s_{21} + s_{22} + s_{23}$$

$$\beta_3 = s_{31} + s_{32} + s_{33} \qquad \beta = \beta_1 + \beta_2 + \beta_3$$

and are given below in the Table VI.

TABLE VI

Unit 10^{-13} cm.²/dyne

Substance	β_1	β_2	β_3	β
1 Sodium tartrate	13·6	8·70	4·00	26·3
2 Rochelle salt ..	17·3	9·90	1·37	28·6

5. DISCUSSION OF THE RESULTS

A comparative study of the figures given in Tables IV and V reveals that the values for the elastic constants are slightly higher and therefore the elastic moduli are slightly lower for sodium tartrate than for Rochelle salt.

The elastic constants of Rochelle salt have been measured earlier by Mandell (1928) Hinz (1939) and Mason (1939). The values obtained by them as well as those of the author are entered in Table VII for comparison. The values shown against Cady's name are taken from his book and are considered by him as the best set. The C's are calculated from the set of s's which he accepts and are given below:—

$s_{11} = 51{\cdot}8$ $\quad s_{44} = 86{\cdot}5$ $\quad s_{12} = -22{\cdot}0$

$s_{22} = 34{\cdot}5$ $\quad s_{55} = 320{\cdot}0$ $\quad s_{13} = -17{\cdot}2$

$s_{33} = 32{\cdot}8$ $\quad s_{66} = 114{\cdot}0$ $\quad s_{23} = 13{\cdot}6$

These are more or less Hinz's values converted into the adiabatic ones from his static measurements.

TABLE VII. *Rochelle salt*

Unit 10^{11} dynes/cm.^{2}

Observer	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
Mandell ..	3·47	4·73	8·06	1·64	0·324	1·24	−0·804	3·16	−3·44
Hinz ..	7·34	11·05	10·10	1·04	0·30	0·93	7·575	7·12	8·71
Mason ..	4·25	5·15	6·29	1·25	0·304	0·996	2·96	3·57	3·42
Author ..	4·06	5·20	6·40	1·22	0·30	0·95	2·56	3·46	3·20
Cady ..	7·48	11·08	10·29	1·16	0·312	0·88	7·55	7·05	8·55

It is surprising to note that the values especially for C_{11}, C_{22}, C_{33}, C_{12}, C_{13} and C_{23} given by the various workers vary enormously. The author's values are in good agreement with those given by Mason.

Table VIII gives the values of the compressibilities which have been computed from the elastic moduli reported by the different workers and those obtained experimentally by Bridgman.

TABLE VIII

Compressibility	Mandell	Hinz	Mason	Author	Bridgman	Cady
β_1 ..	17·1	13·6	15·4	17·3	13·6	12·6
β_2 ..	40·8	− 0·9	9·3	9·9	27·6	− 0·9
β_3 ..	23·2	2·1	2·0	1·37	19·9	+ 2·0
$\beta = \beta_1+\beta_2+\beta_3$	81·1	14·8	26·7	28·6	61·1	13·7

Here again, one finds many curious discrepancies, the most striking of which is the expansion along the Y direction under a uniform pressure, predicted by the values of Hinz and Cady.

From the existing data alone, it is very difficult to explain the discrepancies, especially because the elastic constants of Rochelle salt are highly influenced by a number of factors. Cady suggests that Hinz's cross constants, especially s_{12}, and s_{23} may be numerically too great. The same reason makes Hinz's cross constants of the type c_{ij} $(i \neq j)$ very high compared to the principal constants C_{11}, C_{22}, C_{33}, some of the former being greater than the principal ones themselves. Though quartz belongs to the trigonal system it is instructive to compare the principal elastic constants of quartz with those of Rochelle salt. Thus in quartz, $C_{11} = C_{22} = 8·75$; $C_{33} = 10·77$

in the same units as above and from Hinz's data for Rochelle salt, the constants of the latter are higher than for quartz. The average elastic constant of quartz obtained by space averaging C'_{33} for all orientations for quartz is about 10·5 and the same for Rochelle salt is about 9·6, a result which cannot be valid considering the softness of the crystal compared with quartz.* The same conclusion follows even if one uses for the calculation the values which Cady considers best.

It can be seen from Table VI that Rochelle salt is slightly more compressible than sodium tartrate which is in conformity with the lower elastic constants of the former. This may be due to the presence of the heavier potassium ion in Rochelle salt analogous to the gradation exhibited by the decreasing elastic constants in the alkali halides with increasing ionic radius. This is corroborated by the fact that the unit cell of Rochelle salt is slightly larger than that of sodium tartrate. The axial ratios of sodium tartrate are $a:b:c = 0{\cdot}7787:1:0{\cdot}3354$ (Groth), while those of Rochelle salt are $a:b:c = {\cdot}8325:1:0{\cdot}4334$ (Cady).

The author expresses his grateful thanks to Prof. R. S. Krishnan for his kind guidance in the work. The author thanks Mr. V. M. Padmanabhan for the loan of the crystals.

6. Summary

The elastic constants of sodium tartrate and Rochelle salt are determined by the ultrasonic method. The results are discussed along with the existing data on Rochelle salt. The constants of sodium tartrate are determined for the first time.

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* The average for all possible orientations is given by

$$\frac{1}{4\pi}\int_{\phi=0}^{\phi=2\pi}\int_{\phi=0}^{\phi=\pi} C'_{33}\sin\theta\, d\theta\, d\phi$$

THE DOPPLER EFFECT IN THE FIELD OF A THICK SPHERICAL SHELL

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1. Introduction

It is well known that the gravitational potential is constant in the cavity of a thick heterogeneous shell of matter, having a distribution of spherical symmetry, and that the gravitational force is consequently nil at each point. The relativistic field of such a shell has been obtained by J. T. Combridge (1926). A more general discussion may be found in a later treatment by A. J. Carr (1933). The relativistic analogue of the classical result of a constant potential in the cavity is found to be in the Euclidean metric representing its space-time. There is however another result which is purely relativistic, having no classical analogue for this gravitational situation. It is the Doppler effect in the cavity. That the Riemannian metric of a gravitational field gives rise to a Doppler effect is a fact that has been known since the early days of general relativity. In the present note we consider an observer situated within the cavity of a spherical shell and a light source situated outside the shell. The observer, moving as he is in a flat space-time, experiences the shift on account of the conditions of continuity to be satisfied at the boundaries of the shell. Apart from any possible cosmological application of this, we find that the result which has not been explicitly stated before is novel enough to be placed on record here. Moreover the cavity in this case presents the only known example of a Euclidean pocket in a Riemannian space-time. In the relativistic analogue of a thick homœoid of matter, in the cavity of which there is no gravitational force, a similar Euclidean pocket is expected to exist. But this problem, as far as we know, has not yet been worked out. We give here just the few essential details showing how the pocket arises and how the constant of Doppler effect is fixed by the boundary conditions. This constant depends upon the constant L appearing in the following discussion. We find that Combridge's treatment is defective on account of his assumption $L = 1$.

2. The Field

For a shell of radii a and b $(b > a > 0)$ we assume the distribution of matter to be of spherical symmetry and obtain the metric

$$ds^2 = -e^{\lambda}dr^2 - r^2(d\theta^2 + \sin^2\theta d\phi^2) + e^{\nu}dt^2 \qquad (1$$

where, in the usual notation,

$$e^{-\lambda} = 1 - \frac{2}{r} m(r), \tag{2}$$

$$m(r) = \frac{4\pi G}{c^2} \int_a^r T_4^4 r^2 dr, \tag{3}$$

$$e^{\nu} = L\left(1 - \frac{2}{r} m(r)\right) e^{\int_a^r F(r)\, dr}, \tag{4}$$

$$F(r) = \frac{8\pi G}{c^2} \cdot r\left(1 - \frac{2}{r} m(r)\right)^{-1} (T_4^4 - T_1^1), \tag{5}$$

for $a < r < b$, in the usual notation. L is an arbitrary positive constant which is fixed by the boundary conditions. The only non-zero components of the energy-momentum tensor are T_1^1, T_2^2, T_3^3, T_4^4 and consistency demands that $T_2^2 = T_3^3$. Combridge has taken as the mass equivalent of the distribution,

$$m_1 = \frac{4\pi G}{c^2} \int_a^b T_4^4 r^2 dr. \tag{6}$$

The total energy of the distribution in the shell is

$$\left[e^{-\lambda/2} \cdot \frac{\partial}{\partial r}(e^{\nu/2})\, 4\pi r^2\right]_a^b = 4\pi m_0 \tag{7}$$

according to a formula given by G. K. Patwardhan and P. C. Vaidya (1943). Since T_1^1 vanishes at $r = a$ and $r = b$, we find that m_1 and m_0 are connected by

$$L^{\frac{1}{2}} \cdot e^{\frac{1}{2}\int_a^b F(r)\, dr} \cdot 4\pi m_1 = 4\pi m_0. \tag{8}$$

We can make $m_1 = m_0$ only by taking

$$L = e^{-\int_a^b F(r)\, dr} \tag{9}$$

and thus the continuity of $g_{\mu\nu}$ is ensured at $r = b$, provided we take Schwarzchild's line-element for $r \geqslant b$,

$$ds^2 = -\left(1 - \frac{2m_0}{r}\right)^{-1} dr^2 - r^2 (d\theta^2 + \sin^2\theta d\phi^2) + \left(1 - \frac{2m_0}{r}\right) dt^2. \tag{10}$$

Both Carr and Combridge envisage the case where the integral in (9) vanishes. But it is clear that this takes away the physical interest from the problem. It may be noticed that because Combridge did not introduce L in (4) he did not get the Schwarzchild line-element in the usual form for $r \geqslant b$. We

consider it vital not to restrict L as Combridge has done by putting $L=1$. The continuity of $g_{\mu\nu}$ at $r = a$ gives

$$ds^2 = -dr^2 - r^2(d\theta^2 + \sin^2\theta d\phi^2) + e^{-\int_a^b F(r)\,dr} dt^2 \qquad (11)$$

for $0 \leq r \leq a$.

3. The Doppler Effect

We now see that if a pulse of light starts from a stationary source distant $r >> b$ in the region outside the shell and is received at any stationary point on the radial line* within the cavity, there is a violet-shift as given by

$$\left(1 - \frac{2m_0}{r}\right)^{-1} \frac{\lambda^2}{c^2} = e^{\int_a^b F(r)\,dr} \frac{(\lambda - \delta\lambda)^2}{c^2},$$

or

$$\frac{\delta\lambda}{\lambda} = \tfrac{1}{2}\int_a^b F(r)\,dr - \frac{m_0}{r}, \qquad (12)$$

to the first approximation. For a shell of the mass of the sun and of the thickness of the radius of the sun, the constant positive term on the right in (12) is of the order of 10^{-6}. If the second term is neglected, the Doppler effect may be treated as constant for distant sources of light. It is also clear that if the positions of the source and the observer are interchanged, a red-shift is experienced.

Summary

The relativistic field of a thick spherical shell of matter is worthy of notice inasmuch as it provides the only known example of a Euclidean pocket in a Riemannian space-time. The boundary conditions are used to obtain correct expressions for the metric in different parts of the field and an inaccuracy of Combridge's treatment is removed. The constant of the Doppler effect which is a violet-shift, follows from the boundary conditions in an unforced manner.

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[**Note added in proof.*—It may be noted that Tolman's formula, 116·8 (*Relativity, Thermodynamics and Cosmology*, 1934, p. 289) gives the same result, so far as the pure gravitational effect is concerned, even if the observer is not on the radial line.—V. V. N. and A. P.]

MEASUREMENT OF HIGH ALTITUDE VERTICAL COSMIC RAY INTENSITY, AT NEW DELHI, INDIA, 19° NORTH, GEOMAGNETIC LATITUDE

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Introduction

During the last nine years several experiments have been performed in India between the magnetic latitudes 3° N. to 25° N., to measure the cosmic ray intensity at high altitudes. During 1939–40, Millikan, Neher and Pickering (1942) investigated the total cosmic ray intensity in India using recording electroscopes and G-M counters with a radio-sonde technique. Bhabha and co-workers (1945, 1946) investigated the intensity of the soft and the hard component in aeroplane ascents extending upto 40,000 feet. P. S. Gill (1947), in a similar aeroplane experiment, investigated the production of mesons by non-ionising radiation upto a height of 30,000 feet.

It is very difficult to make a quantitative comparison of data obtained by different workers, using apparatus of different geometry. As Pomerantz (1949) has pointed out, such a comparison is subject to considerable error for several reasons. Principally, the geometrical differences introduce uncertainties in the method of reduction of data on a common scale. In some instances the curves are fitted at high altitudes, in others at sea-level. The change in zenith angle distribution of intensity as a function of altitude may vitiate comparisons based simply upon solid angle corrections, and the results obtained may depend upon the altitude at which the data are normalised.

Bhabha and co-workers, as well as Gill, also found in their aeroplane ascents an anomalous peak and a depression in the normally conceived, smooth intensity-altitude curve for the meson intensity.

A programme was therefore undertaken by the present authors to investigate the latitude effect with a standardised geometry of apparatus. It was also intended to study the significance of the anomalies mentioned above.

Four successful flights were made at New Delhi, magnetic latitude 19° N, on the 15th, 21st, 28th and the 30th of September 1948; the first three without, and the last with 10 cm. of lead absorber. In the last lead flight, data was received only upto 24,000 feet, after which the reception of the cosmic ray data failed, though the flight ascended upto 60,000 feet as indicated by the meteorograph channel. For this reason, the results of this flight will not be discussed in this paper. The flights were made in the afternoon between 1300 and 1400 hours. The flights extended only upto 200 mb. of pressure, owing to the large weight of the apparatus, the restricted amount of hydrogen available at a time, and the small balloons used.

Experimental Procedure

Apparatus.—In each flight, a telescope of four G-M counters in quadruple coincidence was sent up. The geometry of the telescope is given in Fig. 1. The angle subtended by the extreme counters defines a cone making angles of 6° and 25° with the vertical. The counters were made

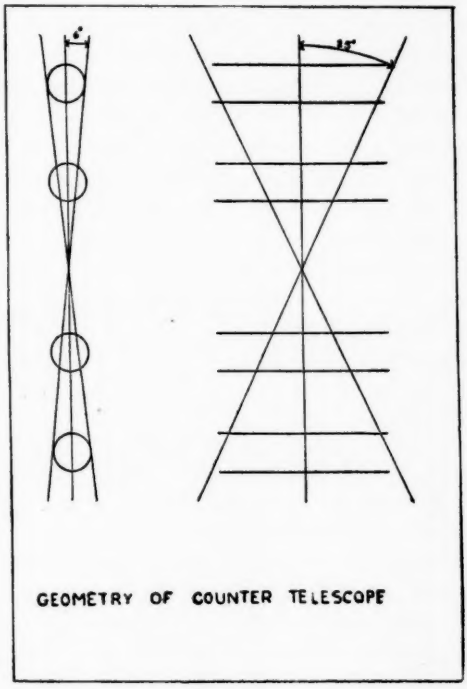

Fig. 1

in the Institute by Mr. H. L. N. Murthy and were of the usual copper-in-glass type filled with a mixture of argon and petroleum ether in a ratio of 4 : 1, to a total pressure of 10 cm. The glass walls were 1·25 mm. thick and the copper cylinders 0·274 mm. thick. Thus, to register a quadruple coincidence, a particle within the above solid angle has to penetrate a total of 3·68 gm./cm.^{2} (1·96 gm./cm.^{2} of glass and 1·72 gm.cm.^{2} of copper).

The quadruple coincidences were transmitted to the ground station over one ultra-high frequency carrier. The pressure and the temperature of the apparatus enclosure were also simultaneously transmitted over another carrier to the ground. Both these data are recorded at the ground station on a continuously moving paper tape, on which a time trace is also recorded throughout the experiment. Details regarding the complete balloon-borne equipment and the ground station equipment are published by R. P. Thatte (1949). Therein, it is shown that the finite resolving times of the various circuits used, introduce very small errors and therefore no corrections have been made in the following data.

The dead-time of our G-M counters was found to be of the order of $3{\cdot}7 \times 10^{-4}$ sec., as measured on a circuit similar to that described by Stevar (1942). This dead-time introduces an appreciable error as the counter is subjected to high counting rates at high altitudes. For a flux of N particles per unit of time and a dead-time τ_0, the efficiency of a counter will be $\epsilon = 1 - N\tau_0$. For a telescope of 'n' fold coincidences, the overall efficiency of the telescope will be ϵ^n. Using Millikan's data for the cosmic ray intensity with a single counter, near the latitude of our experiment, we estimate that the maximum counting rate of a single counter will be about 50 times the rate at sea-level. For our counters, N at ground was 3 counts per second, which at the maximum would be 150 counts per second. The overall efficiency of our quadruple coincidence telescope would therefore be $(1 - 3{\cdot}7 \times 10^{-4} \times 3)^4$ and $(1 - 3{\cdot}7 \times 10^{-4} \times 150)^4$, *i.e.*, 0·9954 and 0·795 at the ground and the maximum counting rate respectively, requiring our observed data for these levels to be multiplied by 1·005 and 1·255. Thus the correction, though very small near the ground, increases with altitude. For lack of data on the intensity given by a single counter with altitude, for the latitude of our experiment, the correction has not been applied to our data. In future experiments it is proposed to obtain the single counter data in preliminary flights to be able to apply these corrections and also to obtain the single counter intensity data at New Delhi at a later date to correct the data published here.

Free Balloon Flights

In collecting the data by the radio-sonde technique, the rate of ascent has to be decided on from the beginning not only to meet a desired statistical accuracy in a chosen interval of height and time, but also to reach the maximum possible height in a time interval in which the battery voltages remain within their useful operating ranges and the temperature of the apparatus does not fall below the tolerable limit. These two requirements are usually contradictory to each other and a compromise has to be made. Our G-M high tension battery, which had to be assembled just before the ascent, had a working range of only one and a half to two hours, and consequently we had to reach the maximum possible height in this time.

The weights of our complete balloon-borne equipment using telescopes, with and without 10 cm. lead absorber, were 22 k. gm. and 30 k. gm. respectively. Indian made latex balloons, type NR-220 made by the Nagpur Rubber Industries, were used. The performance of these balloons is equivalent to that of American, Darex J-800 balloons.

With the amount of hydrogen available to us for one ascent from a set of eighteen army portable hydrogen generators (utilising the ferro-silicon-caustic soda reaction), the maximum number of balloons that could be used at a time was limited. With the abovementioned weights of our equipment, with free lifts of 2500 to 3000 gm. per balloon, and the maximum possible number of these that could be used per ascent, our apparatus could only reach altitudes upto 40,000 feet.

Temperature Control

It is well known that G-M counters filled with organic quenching vapours have an appreciable temperature coefficient at low temperatures. The battery voltages also fall appreciably when the temperature is near 0° C. To study the anomalous hump and the depression in the 500 mb. region, reported by Bhabha and Gill, we wanted a good temperature control of our apparatus, since the air temperature at these pressures is near 0° C.

The temperature control was obtained by the " green house " effect possible in a daytime flight. In a few preliminary flights the proper method of securing the radiation balance was found. For the size of the bamboo cage required by our cosmic ray apparatus, the ratio of the transparent to reflecting area of the covering cellophane was varied. It was found that even with no reflectors the temperature inside the enclosure fell below 0° C. during an ascent. Finally a double jacket, of violet cellophane inside, and clear cellophane outside, was found to give an adequate temperature control.

Fig. 2 shows the performance of the different enclosures in some preliminary ascents made at Poona in the month of June 1948. The double cellophane enclosure flight shows a temperature + 32° C., even at a pressure of 150 mb.

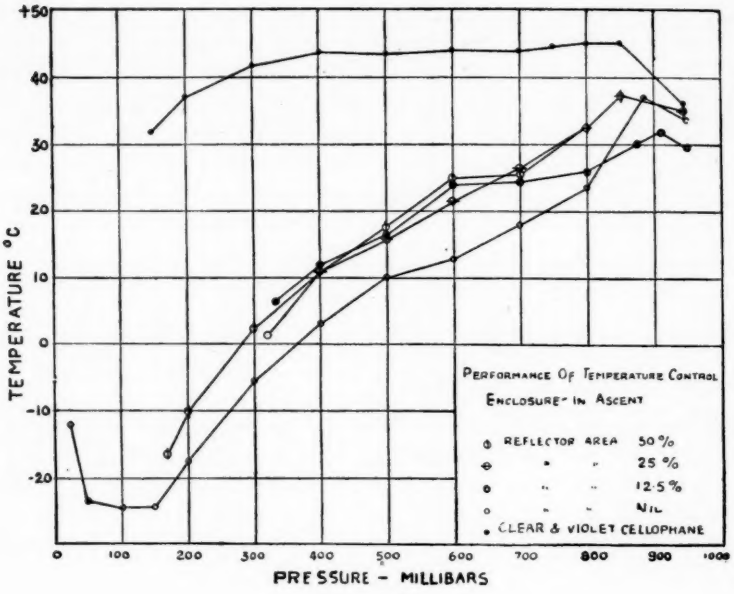

FIG. 2

THE EXPERIMENTAL DATA

The cosmic ray counts are recorded continuously on a tape while the apparatus continues to ascend. The usual method of tabulating the data is to count the total number of counts obtained between two pressures, divide this number by the corresponding time to obtain the mean counting rate in the interval, and then ascribe this mean rate to the mean pressure value in the interval. There is a certain latitude in the choice of an interval during which the counts are lumped together. If the intervals are large there is greater error in determining the mean pressure in the interval, if they are small the statistical fluctuation of the counts in the interval is larger. The statistical fluctuations which are usually large in the lower levels, make it difficult to fit a smooth curve to the points by eye. In applying some of the rigorous statistical methods of analysis for finding out if the deviation of a point from the smooth curve is due to fluctuation or is significant, it is also necessary to assume some relation between the intensity and pressure,

based on either some theoretical hypothesis or on previous experimental data.

The general trend of the total vertical cosmic ray intensity as a function of pressure is known fairly accurately from the results already published. The data of Biehl, Montgomery and others (1948), may be taken as a good representation, since the experimental errors are less than 1%. Taking the curve for the data at Rapid City (Fig. 3 in the paper just mentioned), we decided to find the equation which would best represent it. We tried the following equations:

$$Y = A + Bx + Cx^2 + Dx^3 \tag{1}$$

$$Y = A + B(\log x) + C(\log x)^2 + D(\log x)^3 \tag{2}$$

$$\log Y = A + B(\log x) + C(\log x)^2 + D(\log x)^3, \tag{3}$$

where Y is the intensity (counting rate) and x is the pressure in millibars.

The methods of polynomial fitting are very much simplified if the independent variable is chosen at equal intervals. In calculating polynomial values for equations (1), (2) and (3) we chose x and log x respectively, at equal intervals and found out from the above curve the intensities at the pressure corresponding to the interval chosen.

The calculation of a polynomial is further simplified if it suffices to know the values of the polynomial at the points selected. Fisher (1946) in section 28 of his book deals with these simplified arithmetical methods of curve fitting, which we have used.

It was found out that a polynomial of type (3) satisfied the above data of the chosen curve very well. It was further varified, that the same polynomial still gave the best fit if only a portion of the curve was taken. For example, observations upto 1·6 metres of water equivalent of pressure were taken from the curve and still a good fit obtained. This we did with a view to satisfying ourselves that such a polynomial would be satisfactory for our data, which reached a pressure just near the maximum of the intensity-pressure curve. Fig. 3 shows the Rapid City data in solid curve. The solid points represent the values of the polynomial calculated to give the best fit to the whole set of observations, while the open circles are the calculated values of the polynomial fitting the data below the maximum. As a further check, this polynomial (a cubic in log of intensity versus log of pressure) was calculated for a few other observations, and particularly for the observations of Neher and Pickering (1942) at 17° N., in India. It was found that this particular polynomial represented all the observations very well.

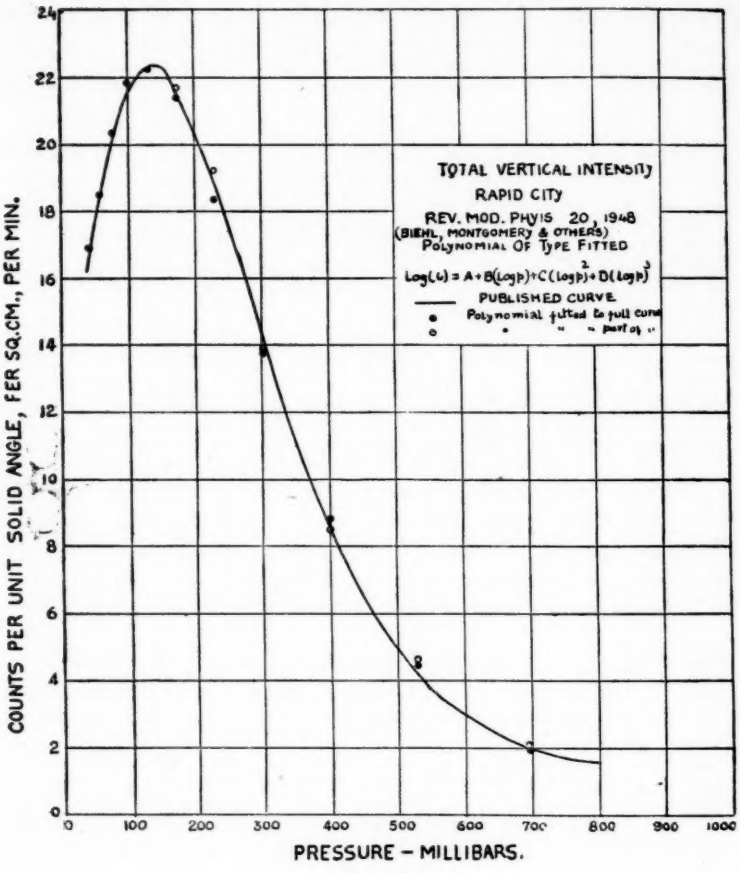

FIG. 3

We therefore fitted the above polynomial of type (3) to the data of our successful flights for the total cosmic ray intensity. We had first to choose equal log pressure intervals. This interval was made as small as possible without reducing the number of counts in each interval so much as to increase the statistical fluctuations; also, a choice of a large interval would obscure the significance of any observed deviations.

Since, in our tape recording, the pressure readings were recorded once during each cycle of the meteorograph, to find out the pressures corresponding to a required log p interval, time *versus* pressure interpolation curves were drawn on semi-log paper, from the recorded pressures and the time

marking on the tape. The scale of the time axis was chosen to read accurately to 0·01 minute. From these curves the required pressure points were marked on the tape and the number of counts and the time duration was measured to calculate the rate. Since the relation of the log pressure against height in the atmosphere is a straight line, the average counting rate is taken to represent the rate at the average height in the interval (not the average pressure in the interval). The mean of the log p values for an interval was therefore shown against the average rate calculated.

In Tables I, II and III the data for our three flights are shown with equal selected intervals of log (p). It will be seen that starting with the

TABLE I

Pressure mb. of selected points p	Log p	Diff. log p	Mean of log p of interval	Diff. mean log p	Pressure mb. at mean of log p	Counts in interval	Time of interval minutes	Counting rate at the average of int. counts per min.
Surface 970·0	2·9868		2·9868		970·00	85	120·00	0·7083
		0·0214		0·0429				
923·4	2·9654							
		0·0429	2·94395	0·0429	879·0	6	4·66	1·2876
836·6	2·9225							
		0·0429	2·90105	do	796·4	10	6·57	1·5221
757·8	2·8796							
		do	2·85815	do	721·4	6	5·52	1·0870
686·6	2·8367							
		do	2·81525	do	653·6	4	5·15	0·7767
622·0	2·7938							
		do	2·77235	do	592·1	18	5·92	3·0405
563·5	2·7509							
		do	2·72945	do	536·4	12	3·57	3·3613
510·5	2·7080							
		do	2·68655	do	486·0	16	5·22	3·0651
462·5	2·6651							
		do	2·64365	do	440·2	23	5·39	4·2672
419·0	2·6222							
		do	2·60075	do	398·8	21	4·56	4·6053
379·6	2·5793							
		do	2·55785	do	361·3	25	4·52	5·5310
343·9	2·5364							
		do	2·51495	do	327·3	29	4·25	6·8235
311·6	2·4935							
		do	2·47205	do	296·6	28	3·67	7·6294
282·2	2·4506							
		do	2·42915	do	268·6	51	5·02	10·1594
255·7	2·4077							
		do	2·38625	do	243·4	60	5·82	10·3093
231·6	2·3648							
		do	2·34335	do	220·5	50	5·26	9·5057
209·8	2·3219							
		do	2·30045		199·7	125	12·1	10·3306
191·1	2·2790							

Observations for total vertical intensity measurement ascent at New Delhi. 19° N. (Magn.), India. Time of release 1·50 P.M. Preassure-time interpolation has been done to obtain the counting rates at equal intervals of log (p) to facilitate the computation of polynomial.

TABLE II

Pressure mb. of selected point p	Log p	Diff. log p	Mean of log p of interval	Diff. of mean log p	Pressure mb. at mean of log p	Counts in interval	Time of interval minutes	Counting rate at the average of int. counts per min.
Surface 983·0	2·9926		2·9926		983·00	106	150	0·7067
		0·02135		0·0427				
936·1	2·97125							
		0·0427	2·9499		891·0	1	2·1	0·4762
848·4	2·92855			0·0427				
		do	2·9072		807·4	3	2·92	1·0274
769·0	2·88585			do				
		do	2·8645		731·9	4	2·80	1·4285
696·9	2·84315			do				
		do	2·8218		663·4	10	4·05	2·4691
631·7	2·80045			do				
		do	2·7791		601·3	6	3·74	1·6043
572·5	2·75775			do				
		do	2·7364		545·0	9	3·63	2·4793
518·9	2·71505			do				
		do	2·6937		494·0	16	3·95	4·0506
470·3	2·67235			do				
		do	2·6510		447·0	12	4·47	2·6846
426·3	2·62965			do				
		do	2·6083		405·8	22	3·43	6·4140
386·4	2·58695			do				
		do	2·5656		367·8	29	3·34	8·6826
350·1	2·54425			do				
		do	2·5229		333·4	32	4·12	7·6699
317·4	2·50155			do				
		do	2·4802		302·1	35	3·49	10·0287
287·7	2·45885			do				
			2·4375		273·8	44	4·34	10·1382
260·7	2·41615							

Observations for ascent on 21st September at New Delhi. 19° N. (Magn.), India. The rates are found at pressures with equal log (p) difference to facilitate polynomial calculations.

surface pressure the first point is taken at half the value of the following intervals. Therefore the mean log p for the interval at which the rates are indicated then fall at equal intervals from the surface point, which then can be included in the calculation of the polynomial values.

From these observations, the values of the counting rate are calculated at the observed points for the polynomial of type (3) discussed above. As a matter of additional curiosity values were also calculated to fit an exponential of the type

$$Y = Ae^{-Bx}, \tag{4}$$

where Y is the counting rate and x the corresponding pressure A and B being constants.

TABLE III

Pressure mb. of selected points p	Log p	Diff. log p	Mean of log p of interval	Diff. mean log p	Pressure mb. at mean of log p	Counts in interval	Time of interval Minutes	Counting rate at the average of int. counts per min.
Surface 982·0	2·9921		2·9921		982·0	102	120·0	0·8500
		0·02125		0·0425				
935·3	2·97085		2·9496		890·4	3	3·95	0·7594
		0·04250		0·0425				
848·0	2·92835		2·9071		807·4	8	5·89	1·3582
		0·0425		do				
769·0	2·88585		2·8646		732·1	3	4·70	0·6382
		do		do				
697·2	2·84335		2·8221		663·9	8	6·16	1·2987
		do		do				
632·3	2·80085		2·7796		602·0	8*	6·04	1·3245*
		do		do				
573·3	2·75835		2·7371		545·9	15*	5·57	2·6929*
		do		do				
519·9	2·71585		2·6946		495·0	26	4·82	5·39241
		do		do				
471·4	2·67335		2·6521		448·8	32	4·86	6·5843
		do		do				
427·5	2·63085		2·6096		407·0	39	4·81	8·1081
		do		do				
387·7	2·58835		2·5671		369·1	39	4·41	8·8435
		do		do				
351·5	2·54585		2·5246		334·8	53	4·69	11·3006
		do		do				
318·7	2·50335		2·4821		303·5	57	4·76	11·9747
		do		do				
289·0	2·46085		2·4396		275·2	45	4·22	10·6635
		do		do				
262·0	2·41835		2·3971		249·6	91	7·40	12·2972
		do		do				
237·6	2·37585		2·3546		226·2	177	13·77	12·8540
215·4	2·33335							

Observations for ascent on 28th September at New Delhi, India. 19° N. (Magn.). Rates are found at pressures with equal differences of log (p).

* Some counts were lost in 602·0 and 545·9 mb. interval due to reception failure; the true rate would then be higher than indicated above.

Tables IV, V and VI give the values from the polynomial and the exponential at the observed points calculated for the three flights. In Figs. 4, 5 and 6 are drawn the observed points and the calculated polynomial and exponential curves. In these figures, at the top are indicated the temperatures inside the apparatus enclosure at corresponding pressure points during the ascent. It will be seen from these curves that the observed points in the regions of 800–400 mb. lie well off the smooth calculated curves for the polynomial and the exponential. To find out whether these deviations are

TABLE IV

Pressure mb.	Observed counts in interval	Time for int. min.	Observed rate counts/m.	Calculated rate counts/min.		Calculated total counts in interval		χ^2	
				Polyn.	Expon.	Polyn.	Expon.	Polyn.	Expon.
Surface 970·0	85	120·00	0·7083	0·8549	0·656	102·588	78·72	3·0153	0·5009
879	6	4·66	1·2876	0·9683	0·904	4·5123	4·2126	0·4904	0·7583
796·4	10	6·57	1·5221	1·1310	1·210	7·4306	7·9497	0·8884	0·5287
721·4	6	5·52	1·0870	1·3540	1·576	7·4740	8·6995	0·2906	0·8376
653·6	4	5·15	0·7767	1·6520	2·001	8·5078	10·3052	2·3834	3·8578
592·1	18	5·92	3·0405	2·0430	2·486	12·0945	14·7171	2·8835	0·7323
536·4	12	3·57	3·3613	2·5470	2·907	9·0927	10·3780	0·9295	0·2535
486·0	16	5·22	3·0651	3·1810	3·612	16·6048	18·8546	0·0220	0·4321
440·2	23	5·39	4·2672	3·9590	4·240	21·3390	22·8536	0·1292	0·0009
398·8	21	4·56	4·6053	4·8790	4·912	22·2482	22·3987	0·0700	0·0873
363·3	25	4·52	5·5310	5·9270	5·533	26·7900	25·0092	0·1196	0·0
327·3	29	4·25	6·8235	7·0490	6·320	29·9583	26·8600	0·0306	0·1704
296·6	28	3·67	7·6294	8·1660	7·042	29·9692	25·8441	0·1293	0·1798
268·6	51	5·02	10·1594	9·1600	7·771	45·9832	39·0104	0·5473	3·6849
243·4	60	5·82	10·3093	9·8950	8·493	57·5889	49·4293	0·1009	2·2605
220·5	50	5·26	9·5057	10·2300	9·206	53·8098	48·4236	0·2697	0·0513
199·7	125	12·1	10·3306	10·0700	9·907	121·8470	119·8747	0·0815	0·2190
				Total χ^2 for all points ..				12·3812	14·5554
				Total χ^2 omitting surface point ..				9·3659	14·0545

Calculated values of the polynomial and the exponential for data of the ascent on 15th September given in Table I. The χ^2 values for the polynomial and the exponential are given.

significant the χ^2 test used in statistics is applied to these points as well as to all other points. In our case, χ^2 is the square of the difference between the observed and the calculated (from the polynomial and the exponential) number of counts divided by the calculated number of counts in the same interval. The last columns of Tables IV, V and VI give the values of χ^2 for the different intervals.

TABLE V

Pressure mb.	Observed counts in interval	Time for int. min.	Observed rate counts/m.	Calculated rate counts/min.		Calculated total counts in interval		χ^2	
				Expon.	Polyn.	Expon.	Polyn.	Expon.	Polyn.
Surface 983	106	150	0·7067	0·428	0·5830	64·2	87·45	27·215	3·9348
891·0	1	2·1	0·4762	0·631	0·7452	1·3251	1·5649	0·0790	0·2039
807·4	3	2·92	1·0274	0·931	0·9610	2·7185	2·8061	0·0291	0·0133
731·9	4	2·80	1·4285	1·296	1·2460	3·6288	3·4888	0·0379	0·0749
663·4	10	4·05	2·4691	1·744	1·618	7·0632	6·5529	1·2210	1·8133
601·3	6	3·74	1·6043	2·295	2·099	8·5833	7·8503	0·7774	0·4361
545·0	9	3·63	2·4793	2·936	2·7110	10·6577	9·8409	0·2578	0·0718
494·0	16	3·95	4·0506	3·671	3·474	14·5005	13·7223	0·1550	0·3780
447·0	12	4·47	2·6846	4·512	4·403	20·1686	19·6814	3·3084	2·9979
405·8	22	3·43	6·4140	5·404	5·501	18·5357	18·8684	0·6474	0·5197
367·8	29	3·34	8·6826	6·384	6·754	21·3226	22·5584	2·7643	1·8394
333·4	32	4·12	7·6699	7·421	8·121	30·5745	33·4585	0·0664	0·0635
302·1	35	3·49	10·0287	8·512	9·528	29·7069	33·2527	0·9431	0·0918
273·8	44	4·34	10·1382	9·635	10·870	41·8159	47·1758	0·1140	0·2137
				Total χ^2 for all points ..				37·6185	12·6521
				Total χ^2 excluding surface ..				10·4035	8·7175

Calculated polynomial and exponential values for counting rate of the ascent data in Table II, with respective values of χ^2.

Reference to Fisher and Yates' probability tables for χ^2 for various degrees of freedom, gives us then the significance of any observation. The total of χ^2 for all observations gives the goodness of fit.

TABLE VI

Pressure mb.	Observed counts in interval	Time of interval	Observed rate counts/m.	Calculated rate counts/min.		Calculated total counts in terval		χ^2	
				Polyn.	Expon.	Polyn.	Expon.	Polyn.	Expon.
Surface 982	102	120·0	0·8500	0·8130	0·462	97·56	55·44	0·2020	74·9475
890·4	3	3·95	0·7594	0·8015	0·700	3·1659	2·7650	0·0086	0·1990
807·4	8	5·89	1·3582	0·8804	1·020	5·1856	6·0078	1·5274	0·6606
732·1	3	4·70	0·6382	1·057	1·437	4·9679	6·7539	0·7795	2·0864
663·9	8	6·16	1·2987	1·362	1·957	8·3899	12·0551	0·0181	1·3640
602·0	8	6·04	1·3245	1·848	2·591	11·1619	15·6439	0·8956	8·6211
545·9	15	5·57	2·6929	2·589	3·344	14·4207	18·6261	0·0232	0·7059
495·0	26	4·82	5·3941	3·678	4·213	17·7280	20·3067	3·8597	1·5962
448·8	32	4·86	6·5843	5·198	5·197	25·2623	25·2574	1·7970	1·7999
407·0	39	4·81	8·1081	7·168	6·284	34·4781	30·2260	0·5930	2·5469
369·1	39	4·41	8·8435	9·471	7·464	41·7671	32·9162	0·1833	1·1244
334·8	53	4·69	11·3006	11·75	9·071	55·1075	42·5430	0·0805	2·5703
303·5	57	4·76	11·9747	13·47	10·05	64·1172	47·8380	0·7900	1·7547
275·2	45	4·22	10·6635	13·96	11·43	58·9112	48·2346	3·2849	0·2169
249·6	91	7·40	12·2972	12·85	12·83	95·0900	94·9420	0·1759	0·1636
226·2	177	13·77	12·8540	10·31	14·28	41·9687	196·6356	8·6441	1·9607
				Total χ^2 all points ..				22·8628	102·3190
				Total χ^2 omiting surface point ..				22·6608	27·3115

Calculated polynomial and exponential values for counting rate of the ascent data in Table III, with respective values of χ^2.

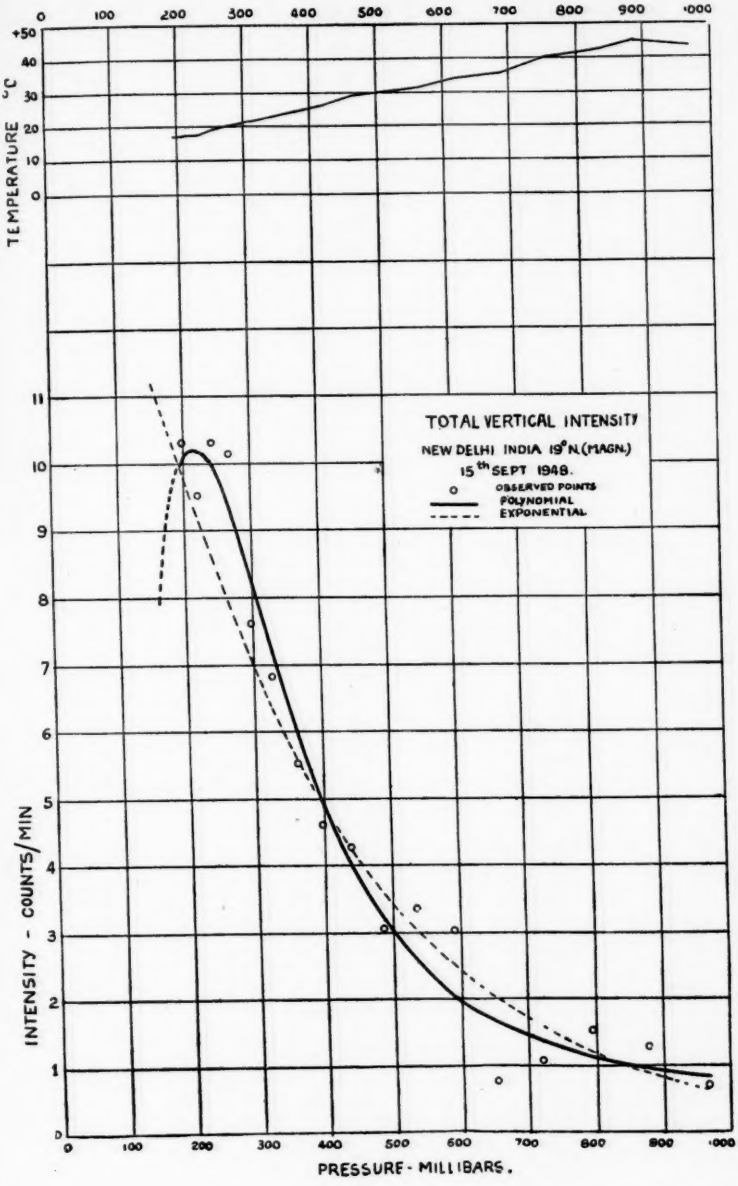
TOTAL VERTICAL INTENSITY
NEW DELHI INDIA 19°N.(MAGN.)
15th SEPT 1948.
OBSERVED POINTS
POLYNOMIAL
EXPONENTIAL
TEMPERATURE °C
INTENSITY - COUNTS/MIN
PRESSURE - MILLIBARS.

FIG. 4

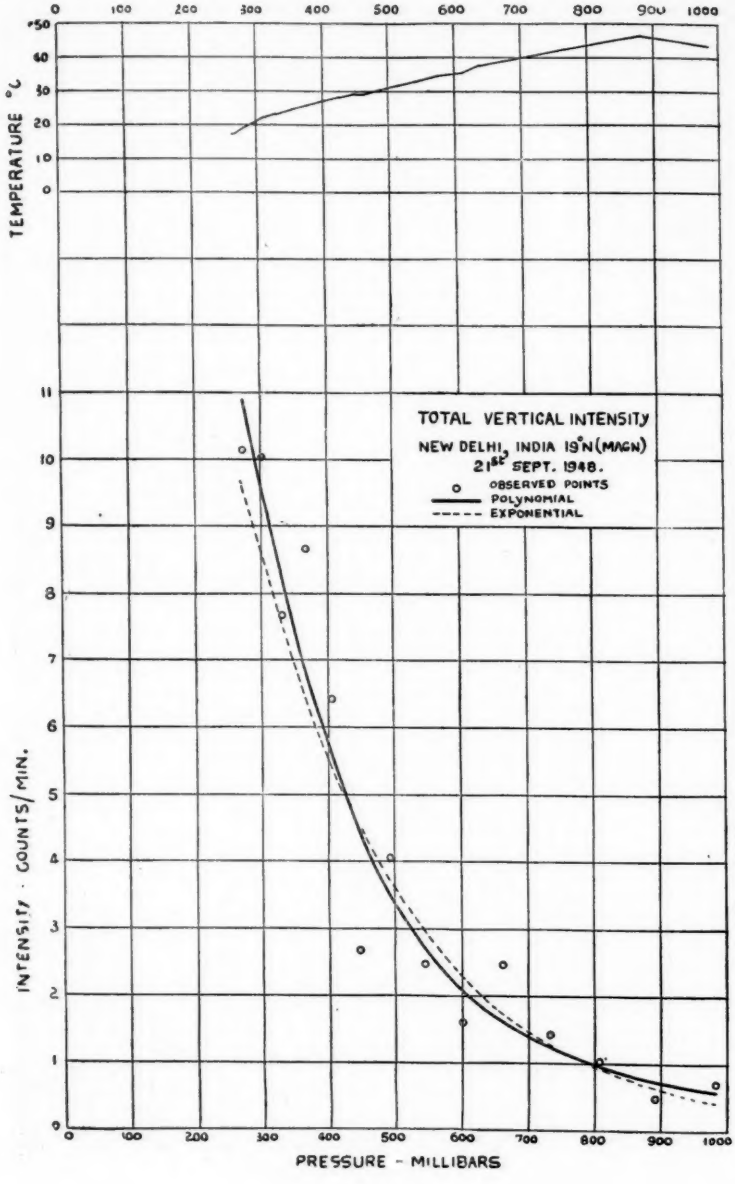
TEMPERATURE °C
INTENSITY - COUNTS/MIN.
PRESSURE - MILLIBARS
TOTAL VERTICAL INTENSITY
NEW DELHI, INDIA 19°N (MAGN)
21ST SEPT. 1948.
OBSERVED POINTS
POLYNOMIAL
EXPONENTIAL

FIG. 5

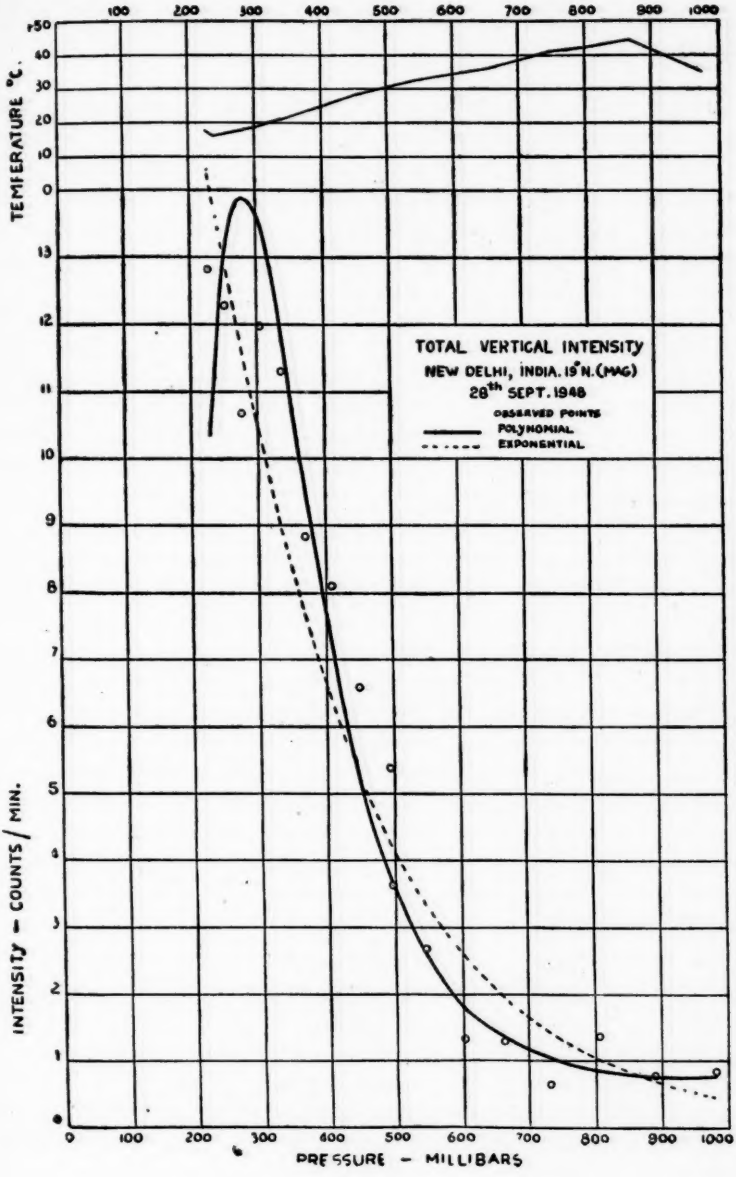
TEMPERATURE °C.
INTENSITY - COUNTS / MIN.
PRESSURE - MILLIBARS
TOTAL VERTICAL INTENSITY
NEW DELHI, INDIA. 19°N. (MAG)
28th SEPT. 1948
OBSERVED POINTS
POLYNOMIAL
EXPONENTIAL

FIG. 6

A4

Discussion of Results

Ascent on 15th September 1948

From Tables IV and Fig. 4 the goodness of fit of the polynomial and the exponential to the seventeen observed points can be judged. From Table IV the fit of the curve can be better judged by examining the sum of the values of χ^2 for the whole curve. Thus, for the polynomial, the four coefficients of the cubic have been chosen to give the best possible fit and the number of "degrees of freedom" left is $17 - 4 = 13$. For the exponential, the constants to be calculated are two, giving $17 - 2 = 15$ degrees of freedom. The sum of χ^2 for the polynomial and the exponential are 12·3812 and 14·5554 respectively. Reference to the Fisher and Yates' tables for the probability of χ^2 for various degrees of freedom, shows that for both the polynomial and the exponential the probability is 50%, and the overall fit is good. However upon examining the individual values of χ^2 we see that the surface point where the rate was determined from two hours observation, gives the value of χ^2 as 3·0153 for the polynomial, which from tables show a probability of slightly more than 5% showing that at this value the polynomial does not fit the surface observation. If we omit the surface point we find from the sum of the residual χ^2 values and for the new degrees of freedom ($16 - 4 = 12$ for the polynomial and $16 - 2 = 14$ for the exponential) the probability of total χ^2 is 70% for the polynomial. There is no improvement in the value for the exponential which still shows 50% probability. Therefore if we omit the surface point, the polynomial fits the observed points better than exponential. For the individual values of χ^2 for the exponential, the points at 296·6 and 243·4 show large values of χ^2 giving about 5% probability. This is self-explanatory, since if the curve were to have a hump as is known, an exponential would give high values of χ^2 for points on the two sides of the saddle points. Comparison of the χ^2 values for the other two ascents in Tables V and VI also indicate the same conclusion.

If we then assume that the polynomial is a better fit for the observed points we find that points corresponding 653·6 and 592·1 mb. also show a high value of χ^2; these do not, however, show the points, as statistically significant. However, these points are very nearly in the same pressure regions where Bhabha and co-workers (1947) found significant aberration in their aeroplane ascent, where they suspect a hump at 511 mb. and depression between 650 and 700 mb. The points in our Fig. 4 also have a tendency to show a hump and a depression in these regions.

Ascent on 21st September

A similar examination of the data for the ascent on 21st shows, from Table V and Fig. 5, that for the total fit the polynomial is the better of the two. Individual χ^2 value show that both these curves fit the surface points poorly. Omitting the surface point gives equal probability for both. This is clear since in this ascent, data were not obtained beyond the saddle point. Here the individual χ^2 values in the regions between 500 and 700 mb. do not show high values of χ^2 as in previous flight, It may be, that, because of the higher rate of ascent used in this flight the statistical weights of the points was low compared to the previous flight. An eye examination of the observed points however does give an indication of a hump and depression in those regions.

Ascent on 28th September

For the data of the flight on the 28th from Tables III, VI and Fig. 6, we can see that for the overall fit the polynomial is the better of the two. However, during this flight some data were lost due to reception failure in both the 602·0 and 545·9 pressure intervals. If recorded, they would have given larger counting rates at both these points and would again have indicated a hump and a depression at about the same regions discussed under the flight on 15th (Tables IV and Fig. 4).

Lastly, we normalised the observations of the 21st and 28th September flights, to the flight on 15th September at ground values, where the counting rates were observed for over 2 hours. In Fig. 7 are shown these normalised values for these three flights. Polynomial values of type (3) used before have been calculated for these fresh normalised observations and are drawn for these three flights. The points at the maxima agree fairly well although the maxima for the polynomial do not agree for the 15th and 28th flight either in magnitude or the pressure of the maxima. However, as Janossy (1948) has shown, in order to get the counting rate at the top of the order of 10 per minute to agree within 0·1 per minute (*i.e.*, 0·01% of the individual rate) 36,00,00 counts must be recorded at ground level to find the normalising factor which would make the observations agree within 0·01% at the top. We have in these flights only about 200 counts recorded at the ground giving a significance of 30% to the normalization factor and thus giving an agreement of the maximum within these limits for these three normalised values. The deviations of the pressures, where maxima are indicated, can be attributed to the limited pressure accuracy of our meteorograph at these altitudes.

We have also shown in this figure Neher and Pickering's data (1942) (given in Fig. 8, p. 412 in above reference) for a quadruple coincidence

flight made at Agra, India, 17° N. (magnetic) during 1939–40. The values have been normalised at the top at 200 mb. This curve agrees quite well

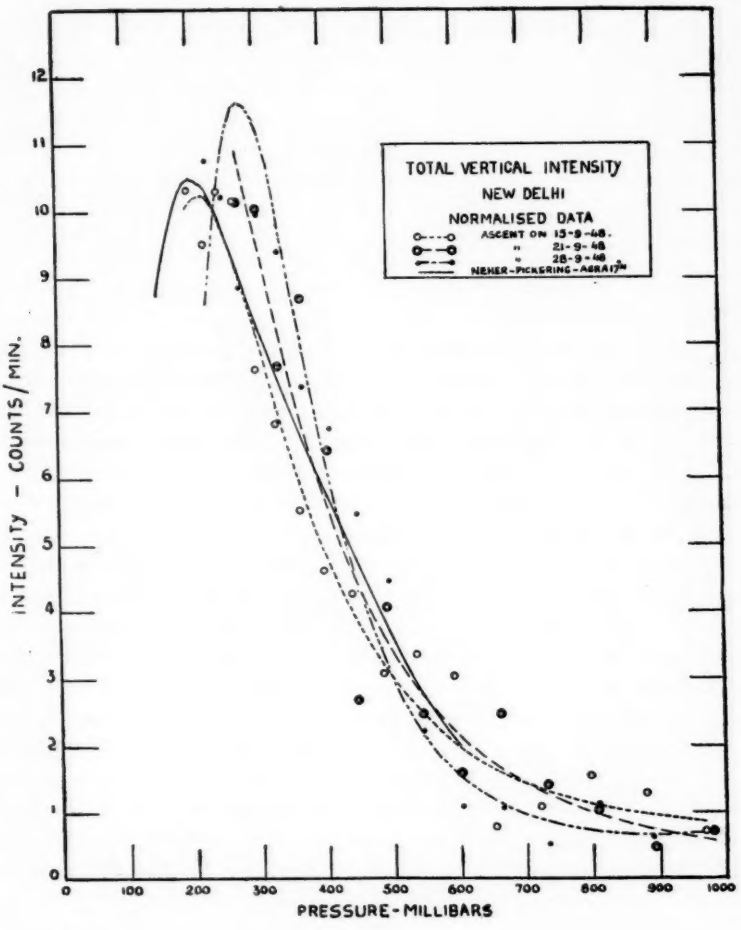

FIG. 7

with data of our three ascents. The pressure at which the maxima occurs agrees very well with the data in the flight of the 15th, showing that our flights just reached the point of maximum cosmic ray intensity. This was at first doubtful as usually in all other data on altitudes *vs.* pressure, the maxima occurs near about the 50–100 mb. regions. It is for this reason

that we first tried to fit an exponential to our set of data, feeling that for the portion of the curve well below the maxima the exponential may give a reasonable fit. However, from the data of Neher and Pickering for the total intensity, the maximum for the intensity for a single counter is reached near about 100 mb., for a double coincidence 180 mb. and for triple and quadruple coincidence flight at 200 mb. in Indian latitudes. Apparently the geometry of the telescope plays a very important part in comparison of the various data as emphasized in our introductory remarks, when stressing the need of a standardised geometry in a latitude-effect study.

The temperature curves for these flights as given in Figs. 4, 5, 6 definitely show that wherever there was an indication of aberrations from the normally conceived intensity-pressure curve, the temperature of the apparatus was quite within the limits where the counting rate was not likely to have been affected. This definitely suggests that the anomalies observed by workers in India are real and are not due to instrumental uncertainties. It is proposed to investigate these regions with better statistical accuracy, by using a telescope with larger counting rate with an increased sensitive area and slower rates of ascent, in special flights intended to reach only upto 400 mb. level in the maximum possible time.

Summary

Using the radio-sonde technique, three high altitude balloon flights were made at New Delhi 19° N. (Mag.) to measure the total vertical intensity to heights upto 40,000 feet (200 mb.). It has been found that the intensity *vs.* pressure curve for the total intensity as reported by other workers is well represented by a third degree polynomial of the log (intensity) against log (pressure). There is good agreement between our three flights when normalised to the same reading at ground level, and our results are well represented by the same polynomial. There is a renewed indication of a hump and a depression in the regions previously reported by Bhabha and co-workers and Gill in their aeroplane ascents, and this cannot be attributed to temperature effect here since the temperature was very well controlled inside the gondola by the 'green house' effect.

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ÜBER DAS MAGNETISCHE MOMENT DES MESONS

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Bekanntlich wird dem Meson der Spin 1 und ein magnetisches Moment vom Betrage $\frac{\epsilon\hbar}{2\mu_0 c}$ zugeschrieben, wo ϵ die Ladung und μ_0 die Masse des Mesons im Ruhezustand, während $\hbar$ die durch 2π dividierte *Planck*sche Konstante und c die Lichtgeschwindigkeit im Vakuum bedeutet. Bekanntlich wurden verschiedene Theorien für die Erklärung solcher Eigenschaften der Mesonen aufgestellt. Speziell wurde das magnetische Moment des Mesons im äusserem elektromagnetischen Felde z. B. von G. *Wentzel*[1]) berechnet. Ausserdem hat *L. de Broglie*[2]) die Methode der Verschmelzung (der Fusion) der Partikeln aufgestellt, mittels welcher er den Spin 1 erklären konnte[3]. Es fehlt aber—soweit mir bis jetzt bekannt—die Ableitung des magnetischen Momentes im Rahmen der *de Broglie*—schen Methode der Fusion und dies ist die Aufgabe dieser Abhandlung, wo gezeigt wird, wie man mittels der *Darwin*schen Methode der Wellenpakete das magnetische Moment des Mesons ausserhalb des Feldes deduzieren kann.

Als vierreihige quadratische hermitische Matrizen, auf die wir die Methode der Fusion der Matrizen anwenden werden, wählen wir

$$\alpha_1 = \begin{Vmatrix} 0 & 0 & 0 & i \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -i & 0 & 0 & 0 \end{Vmatrix} \quad \alpha_2 = \begin{Vmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & 1 \\ i & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{Vmatrix} \quad \alpha_3 = \begin{Vmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{Vmatrix} \quad \alpha_4 = \begin{Vmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{Vmatrix} \tag{1}$$

und überzeugen uns leicht, dass dieselben den *Diracschen* Bedingungen

$$\alpha_\beta \alpha_\gamma + \alpha_\gamma \alpha_\beta = 2\delta_{\beta\gamma} \cdot 1 \qquad (\beta, \gamma = 1, 2, 3, 4) \tag{2}$$

genügen. Diesen Matrizen entsprechende *Dirac*sche Gleichungen der beiden Partikeln, welche wir durch die Fusion zu einer Einheit verreinigt denken, lauten für die erste Partikel

$$\begin{aligned}
&\frac{\hbar}{i}\left\{i\frac{\partial\Psi'_4}{\partial x} - i\frac{\partial\Psi'_3}{\partial y} + \frac{\partial\Psi'_3}{\partial z}\right\} - \frac{\mu_0}{2}c\Psi'_1 + \frac{\hbar}{ic}\frac{\partial\Psi'_1}{\partial t} = 0 \\
&\frac{\hbar}{i}\left\{\frac{\partial\Psi'_3}{\partial x} + \frac{\partial\Psi'_4}{\partial y} - i\frac{\partial\Psi'_4}{\partial z}\right\} - \frac{\mu_0}{2}c\Psi'_2 + \frac{\hbar}{ic}\frac{\partial\Psi'_2}{\partial t} = 0 \qquad (3a) \\
&\frac{\hbar}{i}\left\{\frac{\partial\Psi'_2}{\partial x} + i\frac{\partial\Psi'_1}{\partial y} + \frac{\partial\Psi'_1}{\partial z}\right\} + \frac{\mu_0}{2}c\Psi'_3 + \frac{\hbar}{ic}\frac{\partial\Psi'_3}{\partial t} = 0 \\
&\frac{\hbar}{i}\left\{-i\frac{\partial\Psi'_1}{\partial x} + \frac{\partial\Psi'_2}{\partial y} + i\frac{\partial\Psi'_2}{\partial z}\right\} + \frac{\mu_0}{2}c\Psi'_4 + \frac{\hbar}{ic}\frac{\partial\Psi'_4}{\partial t} = 0
\end{aligned}$$

und für die zweite Partikel

$$\begin{aligned}
&\frac{\hbar}{i}\left\{\frac{\partial \Psi''_4}{\partial x} - i\frac{\partial \Psi''_3}{\partial y} + \frac{\partial \Psi''_3}{\partial z}\right\} - \frac{\mu_0}{2} c\Psi''_1 + \frac{\hbar}{ic}\frac{\partial \Psi''_1}{\partial t} = 0 \\
&\frac{\hbar}{i}\left\{\frac{\partial \Psi''_3}{\partial x} + \frac{\partial \Psi''_4}{\partial y} - i\frac{\partial \Psi''_4}{\partial z}\right\} - \frac{\mu_0}{2} c\Psi''_2 + \frac{\hbar}{ic}\frac{\partial \Psi''_2}{\partial t} = 0 \qquad (3b) \\
&\frac{\hbar}{i}\left\{\frac{\partial \Psi''_2}{\partial x} + i\frac{\partial \Psi''_1}{\partial y} + \frac{\partial \Psi''_1}{\partial z}\right\} + \frac{\mu_0}{2} c\Psi''_3 + \frac{\hbar}{ic}\frac{\partial \Psi''_3}{\partial t} = 0 \\
&\frac{\hbar}{i}\left\{-i\frac{\partial \Psi''_1}{\partial x} + \frac{\partial \Psi''_2}{\partial y} + i\frac{\partial \Psi''_2}{\partial z}\right\} + \frac{\mu_0}{2} c\Psi''_4 + \frac{\hbar}{ic}\frac{\partial \Psi''_4}{\partial t} = 0
\end{aligned}$$

wo Ψ'_i bzw. Ψ''_i $(i. = 1, 2, 3, 4)$ die Wellenfunktionen darstellen, welche der ersten bzw. der zweiten Partikel gehören. Die Masse beider Partikeln wird gleich genommen und im Ruhezustand mit $\frac{\mu_0}{2}$ bezeichent, da die ruhemasse der durch die Fusion gewonnenen Partikel mit μ_0 bezeichnet wird. Als mittels der Fusion definierte quadratische hermitische Matrizen sechzehnter Ordnung wählen wir mit *L. de Broglie*[4] vier Matrizen a_r und vier Matrizen b_r $(r = 1, 2, 3, 4)$, welche durch die Formeln (für die Elemente der Matrizen)

$$(a_r)_{ik,\,lm} = (\alpha_r)_{il}\,\delta_{km} \qquad (b_r)_{ik,\,lm} = (a_r)_{km}\,\delta_{il} \qquad (4)$$

definiert sind, wo δ_{km} (bzw. δ_{il}) das bekannte Symbol von *Kronecker* bedeutet.

Bekanntlich kann man dann nach *L. de Broglie*[5] die statistiche Dichte γ der elektrischen Ladung des Mesons durch die Gleichung

$$\gamma = \epsilon \sum_{i=1}^{4} \sum_{k=1}^{4} \dot{\Psi}_{ik} \frac{a_i b_k}{2} \Psi_{ik} \qquad (5)$$

und die statistische Dichte $\vec{j}$ des elektischen Stromes durch die Gleichung

$$\vec{j} = \epsilon c \sum_{i=1}^{4} \sum_{k=1}^{4} \dot{\Psi}_{ik} \frac{\vec{a}b_k + \vec{b}a_k}{2} \Psi_{ik} \qquad (6)$$

beschreiben. Zwar hat *L. de Broglie* nur die statistische Teilchendichte und die statistische Dichte des Teilchenstromes angegeben; für die geladenen Mesonen erhalten wir daraus durch die Multiplikation mit der Ladung des Mesons ($\epsilon = \pm e$) die oben angeführten Ausdrücke (5) und (6). Für das Neutretto ergeben die oben angeführten Ausdrücke = O. Hier bedeutet Ψ_{ik} das Produkt der Wellenfunktion Ψ'_i der ersten Partikel und der Wellenfunktion Ψ''_k der zweiten Partikel. Der Unterschied im Vorzeichen zwischen der hiesigen Formel (6) und der Formel von *L. de Broglie* rührt davon

her, dass hier in den *Dirac*schen Gleichungen die zeitliche Ableitung der Wellenfunktion gerade mit umgekehrten Vorzeichen als bei *L. de Broglie*[6] genommen ist.

Wir schreiben jetzt der ersten Partikel als die " grossen " Wellenfunktionen in der Form der *Darwins*chen Wellenpakete

$$\Psi'_{3,4} = A'_{3,4}\, e^{-\frac{(x-v_x t)^2+(y-v_y t)^2+(z-v_z t)^2}{2\sigma'^2}}\, e^{\frac{i}{\hbar}(p_x x+p_y y+p_z z-Ut)} \tag{7a}$$

zu, und der zweiten Partikel die " grossen " Wellenfunktionen

$$\Psi''_{3,4} = A''_{3,4}\, e^{-\frac{(x-v_x t)^2+(y-v_y t)^2+(z-v_z t)^2}{2\sigma''^2}}\, e^{\frac{i}{\hbar}(p_x x+p_y y+p_z z-Ut)} \tag{7b}$$

Hier bedeutet $\vec{p}$ den Impuls und U die Energie der ersten bzw. der zweiten Partikel, welche zusammen die durch die Fusion erzeugte Partikel ergeben, während σ' (bzw. σ'') die " praktische " Ausdehnung des Wellenpaketes der ersten (bzw. der zweiten) Partikel bezeichnet. Die (zwei) " kleinen " Wellenfunktionen der ersten Partikel ergeben sich dann aus den ersten zwei Gleichungen (3*a*) und die " kleinen " Wellenfunktionen der zweiten Partikel ergeben sich aus den ersten zwei von den vier Gleichungen (3*b*). Von den Produkten $\dot{\Psi}_{ik}\frac{\vec{ab}_4+\vec{ba}_4}{2}\Psi_{ik} = \dot{\Psi}_i\dot{\Psi}''_k\frac{\vec{ab}_4+\vec{ba}_4}{2}\Psi'_i\Psi''_k$ in der Gleichung (6) können wir aber in *Newton*scher Näherung alle diejenigen streichen, in welchen mehr als ein Faktor eine " kleine " Wellenfunktion auftritt, also in welchen unter den Indexen i, *k*, *l*, *m* mehr als ein Index kleiner als 3 auftritt.

Jetzt berechen wir auf Grund der Gleichungen (6) und (3*a*, *b*) die einzelnen Ausdrücke $\dot{\Psi}_{ik}\frac{\vec{ab}_4+\vec{ba}_4}{2}\Psi_{ik}$; wir erhalten so für langsame Geschwindigkeiten des Mesons (*d. h.* in *Newton*scher Näherung: $\vec{p} \doteq \frac{\mu_0}{2}\vec{v}$, $U \doteq \frac{\mu_0}{2}c^2$) und für $t = 0$ *z.* B. für die Produkte, welche im Ausdruck für die *x*-Komponente der statistischen Dichte des elektrischen Stromes auftreten

$$i\dot{\Psi}_{31}\Psi_{34} = \frac{1}{\mu_0 c}\dot{A}_3'A_3'A_4''(\dot{A}_4''p_x - \dot{A}_3''p_y + i\dot{A}_3''p_z + \hbar\frac{-i\dot{A}_4''x + i\dot{A}_3''y + \dot{A}_3''z}{\sigma''^2}\, e^{-(x^2+y^2+z^2)\left(\frac{1}{\sigma'^2}+\frac{1}{\sigma''^2}\right)} \tag{8}$$

u. s. w.

Durch Einführung der Ausdrücke (8) in (6) erhält man

$$
\begin{aligned}
j_x = \Big\{ & \frac{2\epsilon}{\mu_0} (\dot{A}_3' A_3' + \dot{A}_4' A_4') (\dot{A}_3'' A_3'' + \dot{A}_4'' A'' {}_4) p_x + \\
& + \frac{\epsilon \hbar}{\mu_0} i \left[\dot{A}_3' A_3' (\dot{A}_3'' A_4'' - \dot{A}_4'' \dot{A}_3'') + \dot{A}_4'' A_4'' (\dot{A}_3' A_4' - A_4' \dot{A}_3') \right] \frac{y}{\sigma'^2} + \\
& + \frac{\epsilon \hbar}{\mu_0} i \left[\dot{A}_3'' A_3'' (\dot{A}_3' A_4' - \dot{A}_4' \dot{A}_3') + \dot{A}_4' A_4' (\dot{A}_3'' A_4'' - \dot{A}_4'' A_3'') \right] \frac{y}{\sigma''^2} - \\
& - \frac{\epsilon \hbar}{\mu_0} \left[- \dot{A}_3' A_3' (\dot{A}_3'' A_4'' + \dot{A}_4'' A_3'') - \dot{A}_4'' A_4'' (\dot{A}_3' A_1' + \dot{A}_4' A_3') \right] \frac{z}{\sigma'^2} - \\
& - \frac{\epsilon \hbar}{\mu_0} \left[- \dot{A}_3'' A_3'' (\dot{A}_3' A_4' + \dot{A}_4' A_3') - \dot{A}_4' A_4' (\dot{A}_3'' A_4'' + \dot{A}_4'' A_3'') \right] \frac{z}{\sigma''^2} \Big\} \times \\
& \times e^{-(x^2 + y^2 + z^2)\left(\frac{1}{\sigma'^2} + \frac{1}{\sigma''^2}\right)} \qquad (9)
\end{aligned}
$$

Setzen wir jetzt voraus, dass $\sigma' = \sigma'' = \sigma$ ist, was um so mehr wahrscheinlich ist, da den beiden Partikeln nach *L. de Broglie* die gleiche Masse zugeschrieben wird, und beachten wir noch, dass

$$
\frac{y}{\sigma^2} e^{-\frac{2}{\sigma^2}(x^2 + y^2 + z^2)} = -\frac{1}{4} \frac{\partial}{\partial y} e^{-\frac{2}{\sigma^2}(x^2 + y^2 + z^2)}, \quad u.s.w.,
$$

so erhalten wir aus der Gleichung (9) endlich die x-Komponente der statistischen Dichte des elektrischen Stromes. Eine völlig analoge Rechnung, welche der Kürze halber ausbleiben kann, führt von (6) zu zwei anderen Komponenten der statistischen Dichte des elektrischen Stromes (*d.h.* zu j_y und j_z).

Aus den Gleichungen für j_x, j_y und j_z könnten wir in analoger Weise schliessen, wie dies aus der Ableitung des magnetischen Momentes des Elektrons (bzw. des Positrons) mittels der *Darwin*schen Methode des Wellenpaketes bekannt ist,[7] dass:

$$
\begin{aligned}
\mathbf{M}_x = & \frac{\epsilon \hbar}{4 \mu_0 c} \left\{ (\dot{A}_3' A_3' + \dot{A}_4' A_4') (\dot{A}_3'' A_3'' - \dot{A}_4'' A_4'') + \right. \\
& \left. + (\dot{A}_3'' A_3'' + \dot{A}_4'' A_4'') (\dot{A}_3' A_3' - \dot{A}_4' A_4') \right\} \int e^{-\frac{2}{\sigma^2}(x^2 + y^2 + z^2)} \, dt \\
\mathbf{M}_y = & \frac{\epsilon \hbar}{4 \mu_0 c} \left\{ (\dot{A}_3' A_3' + \dot{A}_4' A_4') (\dot{A}_3'' A_4'' + \dot{A}_4' A_3'') + \right. \\
& \left. + (\dot{A}_3'' A_3'' + \dot{A}_4'' A_4'') (\dot{A}_3' A_4' + \dot{A}_4' A_3') \right\} \int e^{-\frac{2}{\sigma^2}(x^2 + y^2 + z^2)} \, dt \qquad (10) \\
\mathbf{M}_z = & \frac{\epsilon \hbar}{4 \mu_0 c} \cdot i \left\{ (\dot{A}_3' A_3' + \dot{A}_4' A_4') (\dot{A}_4'' A_3'' - \dot{A}_3'' A_4'') + \right. \\
& \left. + (\dot{A}_3'' A_3'' + \dot{A}_4'' A_4'') (\dot{A}_4' A_3' - \dot{A}_3' A_4') \right\} \int e^{-\frac{2}{\sigma^2}(x^2 + y^2 + z^2)} \, dt
\end{aligned}
$$

ist, wo sich die Integrale auf den ganzen Raum erstrecken. Um die Integrale aus diesen Formeln wegzuschaffen, müssen wir die Normierung mittels der Gleichung (5) für die statistische Dichte der elektrischen Ladung des Mesons ausführen. Unter Anwendung der Matrizen (4) mit Rücksicht auf (1) ergibt die Formel (5)

$$\rho = \epsilon\big(-\dot{\Psi}_{11}\dot{\Psi}_{11} - \Psi_{21}\dot{\Psi}_{21} - \dot{\Psi}_{12}\Psi_{12} - \dot{\Psi}_{22}\Psi_{22} + \dot{\Psi}_{33}\Psi_{33} + \dot{\Psi}_{43}\Psi_{43} + \dot{\Psi}_{34}\Psi_{34} + \dot{\Psi}_{44}\Psi_{44}\big) \tag{11}$$

Von den acht Gliedern auf der rechten Seite können wir hier die erste vier Produkte $\dot{\Psi}_{ik}\,\Psi_{lm}$ streichen, weil sie mit Bezug auf die letzten vier Produkte die lauter "kleinen" Wellenfunktionen (Ψ_1 oder Ψ_2) enthalten. Unter Beachtung der Ausdrücke für die "grossen" Wellenfunktionen (7 *a*) und (*fb*) ausgedrückt durch die *Darwin*schen Wellenpakete erhalten wir noch unter der schon erwähnten Voraussetzung $\sigma' = \sigma'' = \sigma$ leicht aus (11)

$$\int \rho\, dt = \epsilon\,(\dot{A}_3'A_3' + \dot{A}_4'A_4')\,(\dot{A}_3''A_3'' + \dot{A}_4''A_4'')\, e^{-\frac{2}{\sigma^2}(x^2+y^2+z^2)}\, dt = \epsilon \tag{12 a}$$

oder zuletzt

$$\int e^{-\frac{2}{\sigma^2}(x^2+y^2+z^2)}\, dt = \frac{}{(\dot{A}_3'A_3' + \dot{A}_4'A_4')\,(\dot{A}_3''A_3'' + \dot{A}_4''A_4'')} \tag{12 b}$$

Dies in die Gleichungen (10) eingeführt, ergibt dann sofort die drei Ausdrücke für die Komponenten des magnetischen Momentes des Mesons, aus welchen man durch Quadrieren und Summieren leicht erhält

$$|\,\mathfrak{M}\,| = \frac{|\,\epsilon\,|\cdot\hbar}{2\mu_0 c}, \tag{13}$$

wenn man in dem zweifachen Produkt

$$2\,(\dot{A}_3'A_3' + \dot{A}_4'A_4')\,(\dot{A}_3''A_3'' + \dot{A}_4''A_4'')\,[\dot{A}_3''A_3''\dot{A}_3'A_3' + \dot{A}_3''\dot{A}_4'\,(2A_4''A_3' - A_3''A_4') + \dot{A}_4''A_3'\,(2A_3''A_4' - A_4''A_3') + \dot{A}_4''A_4''\dot{A}_4'A_4']$$

welcher in den weggelassenen Zwischenrechnungen vorkommt,

$$\frac{A_3'}{A_4'} = \frac{A_3''}{A_4''} \tag{14}$$

voraussetzt. Dass eine solche Voraussetzung hier annehmbar erscheint, geht schon aus dem Grunde hervor, weil den beiden Partikeln, die sich mittels der Fusion zu einer Einheit vereinigen, die gleiche Masse zugeschrieben wird.

Es erscheint also, dass die *de Broglie*-sche Methode der Fusion der Partikeln (zur Erklärung der Eigenschaften des Mesons und besonders des Spins 1) von grösserer Bedeutung ist als ihr bis jetzt- wie es mir scheint— zugeschrieben wurde. Dasselbe gilt auch für die *Darwin*sche Methode des Wellenpaketes.

Zusammenfassung.—Es wird gezeigt, wie man mittels Anwendung zweier Methoden: der *de Broglie*-schen Methode der Fusion der Partikeln und der *Darwin*schen Methode des Wellenpaketes das magnetische Moment des Mesons ableiten kann.

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